STUDIES IN PYROLYSIS

A thesis by Arnold Golomb, submitted in accordance with the regulations governing the Award of the degree of Doctor of Philosophy in the Faculty of Science of the University of Glasgow.

Acknowledgments

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Studies in Pyrolysis. Part XVII. The Acyl Derivatives and Lactides of Some α-Hydroxy-acids.

By A. Golomb and P.D. Ritchie

PREFACE

Research on the durability of polymeric materials is of growing significance in view of the increasing importance of these synthetic products in our national economy. A knowledge of the mechanisms by which polymers decompose is needed to facilitate accurate prediction of their expected service life, to inhibit degradation more effectively, and to devise better techniques of rapid testing.

Since the beginning of the present century, polymer degradation reactions induced by a variety of agencies have been investigated. Those of industrial interest are usually induced by a combination of several factors, and although heat, light, and oxidation are known to be the most important of these, it is often difficult to unravel the various causes and effects. In the fabrication of commercial materials, for example, high temperatures are encountered in such processes as rolling, moulding, and extruding, during which thermal and oxidative reactions occur simultaneously.

In the research laboratory, such composite reactions can be conveniently broken down into their individual components, and a separate study made of the degradative effects of each.

Of the influences which can induce the degradation of polymers, heat is by far the most widely encountered. Pyrolysis has been described[1] as "the transformation of a compound into another substance or into other substances through the agency of heat alone". The mechanisms of pyrolysis of several linear addition polymers, derived from vinyl-type monomers, have been elucidated by direct measurement

of the changes in molecular weight and rate of evolution of volatile products that occur during the degradation of each polymer. High yields of the original monomer are sometimes obtained from such polymers on pyrolysis.

Since many commercially important polymers are polyesters, much interest has been centred, in these laboratories, on problems of deterioration and thermal instability associated with this class of compounds. With linear polyesters, pyrolytic regeneration of the original monomeric components cannot, of course, occur, since a molecule of water is eliminated from the system for every ester linkage formed during polycondensation. The wide variety of products in the pyrolysate from a given polyester are often too complex for accurate analysis. To overcome this difficulty it has become usual to synthesise and pyrolyse model compounds which bear a close structural resemblance to simple segments of the polyester chain. Subsequent analysis of the products thus obtained usually provides information which can be applied to elucidate the pyrolytic breakdown mechanism(s) of the polyester itself.

Studies of the pyrolysis of relatively simple esters have not only provided information invaluable in the elucidation of polyester breakdown mechanisms, but have in addition furnished the preparative organic chemist with a number of valuable synthetic routes to substances which may be otherwise inaccessible, or very costly (in terms of time and materials) to prepare.

Side effects, such as oxidation and catalysis, have been eliminated as far as possible from the present work by careful control of the experimental conditions. To prevent oxidation, the various pyrolyses have all been done either under an inert atmosphere of carefully purified nitrogen (Part I), or under high vacuum (Part II). All pyrolysis vessels used have been constructed of Pyrex glass, a material which is at present considered to be catalytically inactive toward reactions of the types under investigation.

SYNOPSIS

In Part I of this thesis, the thermal breakdown (vapour phase: ca. 500°) of the lactides obtained from lactic and α-hydroxyisobutyric acid is critically re-examined, with the assistance of some model compounds. The pyrolysis of the lactide of 1-hydroxycyclohexane-carboxylic acid is also studied. The predominating breakdown reaction of all three is a concerted double decarbonylation (yielding carbon monoxide and an aldehyde or ketone) together with minor competing reactions. Reasons are advanced for the failure of the lactides and acyl derivatives of α-hydroxy acids to show major alkyl-oxygen scission to the corresponding unsaturated acids. Reaction mechanisms are discussed.

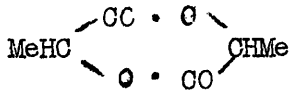
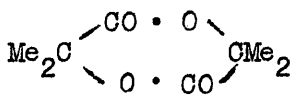
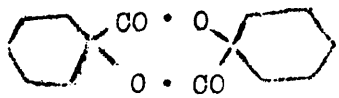
In Part II, the thermal degradation at 220 - 260° of the copolymer poly (diethyl maleate-methyl α-methylacrylate), a suitable model for the cross-linked unsaturated polyester resin, poly(ethylene fumarate-methyl α-methylacrylate), is studied. Mechanisms are advanced for the pyrolytic breakdown reactions of the relatively simple copolymer, which enable predictions to be made about the mode of thermal decomposition of the cross-linking polyaddition chains in the resin. Possible ways of inhibiting thermal degradation of both these materials are considered.

The Appendix to the thesis describes an investigation of the possibility of inducing stereospecific polymerisation of methyl α - methylacrylate by means of circularly polarized ultraviolet light. The results were, however, entirely negative.

LIST OF ABBREVIATIONS

For convenience, the following abbreviations have been extensively used throughout the text of this thesis:

Part I

Symbol	Substance
(I)	
(II)	
(III)	

Part II

(IV)	Poly(ethylene fumarate-methyl α-methylacrylate)
(V)	Poly(diethyl maleate-methyl α-methylacrylate)

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TABLES OF RESULTS

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TABLES OF RESULTS

ILLUSTRATIONS

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PART I

PYROLYSIS OF THE LACTIDES AND ACYL DERIVATIVES OF SOME α-HYDROXY ACIDS

1. INTRODUCTION

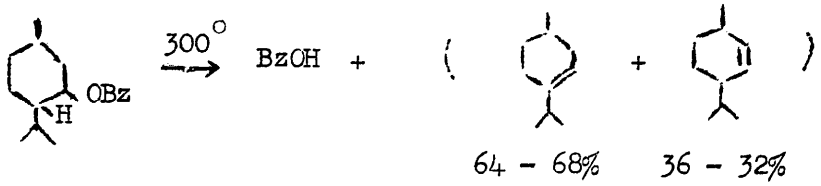
1.1 The Pyrolysis of Simple Esters

Lactides and ∝-acyloxy acids are esters which possess special structural features. Before discussing the results of pyrolysis of these substances, a brief review of all the known routes of pyrolysis of simple esters is presented below. Although many examples given in the early literature report one exclusive route for the thermal breakdown of an ester, it is now known that nearly all esters pyrolyse by two or more primary, competitive routes.

For example, ethyl formate, reported by Engler and Grimm in 1897 to yield ethylene and formic acid by an exclusive route[2], was later shown[3] to decompose thermally by no fewer than three primary competitive routes, ethylene and formic acid being products of the major route:

$$H{\cdot}CO\,OEt \longrightarrow \begin{cases} H \cdot COOH + CH_2{:}CH_2 \\ \frac{1}{2}(CH_2O + CO_2 + Et_2O) \\ CO + EtOH \end{cases}$$

Pyrolysis by an exclusive route has been reported by Barton *et al.*[4] for the thermal decomposition at *ca.* 300° of (-)-menthyl benzoate to benzoic acid and a mixture of the isomeric menthenes, (+)-p-menth-3-ene (64-68%) and (+)-p-menth-2-ene (36-32%).



Muir and Ritchie have more recently confirmed the truly exclusive nature of this thermal breakdown (in the absence of metallic catalysts) by vapour-phase chromatography of the products.[5]

Since secondary pyrolysis of primary products can generally occur, confusion has sometimes arisen in deciding whether a particular product is formed via a primary or a secondary route. A critical survey of the literature indicates that for many pyrolyses, the only products reported were those which were readily identified by existing analytical techniques. Consequently, the literature contains many seemingly anomalous results. It is often possible, however, to explain such fragmentary observations by considering the possibility of non-identification or further pyrolysis of accompanying products. In these laboratories, every product identified in the pyrolysate from a given substance is regarded as a potentially valuable piece of evidence, which may help to build a complete picture of the routes of pyrolytic decomposition.

Hurd[1] has quoted several generalisations on pyrolytic behaviour, but there are so many exceptions to these that they are of little worth in predicting the course of thermal decomposition of a particular substance. It can nevertheless be said that the main factors which determine the course of thermal decomposition of a substance are its molecular structure and the experimental conditions of pyrolysis, in particular, the temperature and contact time in the reaction vessel.

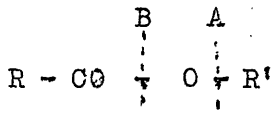
The known routes of pyrolysis of simple esters have been classified, according to the position(s) in the molecule where scission (if any) occurs, use being made of a nomenclature devised by Ritchie.[6] Each type is discussed below; from these established routes it is often possible to predict correctly the general course of thermal decomposition of a particular ester.

The thermal decomposition of an ester may occur in the following ways:

(i) Alkyl-oxygen scission, type A, where scission occurs between the alkyl group and the ether oxygen of the carboxyl group;

(ii) Acyl-oxygen scission, type B, where scission occurs between the carbonyl group and the ether oxygen of the carboxyl group;

These are illustrated below:



(iii) Decarbonylation, decarboxylation, type C, whereby direct elimination of either carbon monoxide or carbon dioxide occurs;

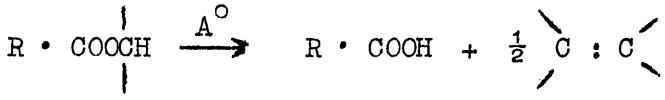
(iv) Disproportionation, type D, where, for example, two identical molecules react to form two other molecules of greater symmetry;

and (v) Rearrangement, type R, which is essentially the thermal isomerisation of an ester.

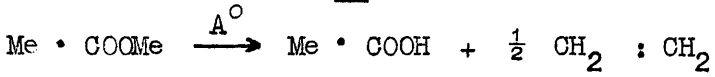
These types of thermal decomposition are discussed below under their respective headings. It is emphasized that most of the reactions cited as examples do not occur alone, but compete with other simultaneous pyrolytic breakdown routes of the ester being discussed.

1.1.1 Alkyl-oxygen Scission (A^{O})

A^{O} scission is a rather uncommon type of scission which has been observed for the pyrolysis of esters which have in the alkyl group an α-hydrogen atom when no β-hydrogen atom is present. Such esters are generally fairly thermostable, and break down only at high temperatures, yielding an acid and an alkene:



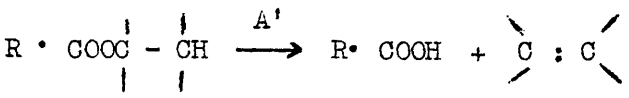
For example, Peytral[7] has found methyl acetate to yield acetic acid and ethylene on pyrolysis at ca. 1100°:



Presumably, the formation of the alkene in A^{O} scission occurs by combination of a pair of methylene-type diradicals, formed as transient intermediates.

1.1.2 Alkyl-oxygen Scission (A')

A' scission is almost invariably the predominating route of pyrolytic breakdown for esters which have in the alkyl group an available β-hydrogen atom. Scission, with migration of the β-hydrogen atom to the carboxyl group, yields an acid and an alkene (or mixture of isomeric alkenes).



Thus, ethyl acetate undergoes pyrolytic conversion[8] to acetic acid and ethylene:

$$AcOCH_2CH_3 \xrightarrow{A'} AcOH + CH_2 : CH_2$$

A' scission of esters is now well established as a convenient general synthetic route to acids and unsaturated compounds, since yields are usually high and side reactions occur only to a relatively minor extent.

Thus, hexadecene has been prepared in excellent yield[9] by the pyrolysis of cetyl palmitate:

$$C_{15}H_{31}CO_2(CH_2)_{15}Me \xrightarrow{A'} C_{15}H_{31}CO_2H + CH_2 : CH(CH_2)_{13}Me$$

Many unsymmetrical secondary esters contain more than one structural kind of β-hydrogen atom, the elimination of each of which by A' scission would produce a different olefin. Thus, for example, sec.- butyl acetate has been reported by Houtman et al.[10] to yield on pyrolysis a mixture of the two formally possible alkenes, but-1-ene and but-2-ene

$$Me \cdot CO_2 \underset{\displaystyle Me}{\underset{|}{CH}} CH_2 Me \xrightarrow{-AcOH} CH_2 : CH\,CH_2\,Me + MeCH : CHMe$$

Two rules have been variously applied to the pyrolysis of such esters, each leading to a different conclusion about the structure of the alkene preferentially formed. The Saytzeff Rule, which governs the dehydrohalogenation of alkyl halides, states that the most highly-branched alkene is mainly produced, whereas the Hofmann Rule, for the thermal dehydration of quaternary ammonium hydroxides, states that the alkene with fewer attached alkyl substituents is favoured.

In the A' scission of (-)-menthyl benzoate, cited above as an example of an exclusive route in pyrolysis, Barton et al[4] have shown the major product to be the more highly branched alkene, (+)-p-menth-3-ene, formed in 64-68% yield. A similar result was observed by McNiven and Read[11] for the pyrolysis of (-)-menthyl acetate. These eliminations clearly follow the Saytzeff Rule.

Bailey et al.,[12] on the other hand, have reported for the pyrolysis of many alkyl acetates the formation of a single alkene by exclusive A' scission according to the Hofmann Rule. Thus, for example, the pyrolysis of 1-methylcyclohexyl acetate was reported to yield as the sole olefinic product methylenecyclohexane:

No 1-methylcyclohex-1-ene was reported, although Birch, Kon, and Norris[13] have shown that in the cyclohexane ring an endocyclic double bond should be more stable than an exocyclic one.

Bailey and several co-workers (inter al. Bailey and Rosenberg),[12] demonstrated that if carbonized deposits were present in the reactor during such a pyrolysis, isomerisation occurred, yielding a mixture of the two formally possible olefinic products. If the reactor was cleaned (by oxidation of the carbonized deposits with nitric acid followed by washing with distilled water) before each pyrolysis, however, only a single olefinic product was observed. A similar result had previously been recorded by Wibaut and van Pelt,[14] who observed no double bond isomerisation of the alkenes formed pyrolytically from a variety of alkyl acetates.

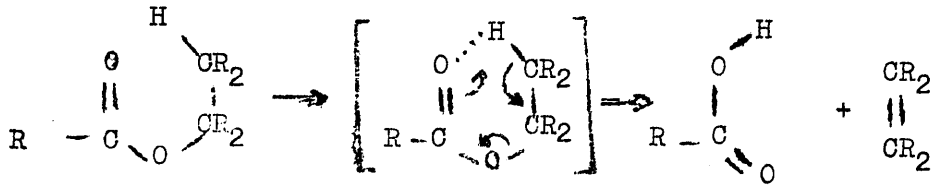
Houtman et al.[10], on the other hand, found that although carbonized deposits in the reaction vessel promoted the onset of pyrolytic decomposition of pure, primary alkyl acetates at ca. 500°, the presence or absence of carbonization had no effect on the ratio of isomeric butenes formed in the pyrolysis of sec. - butyl acetate. Since variation of temperature had no appreciable effect on this ratio either, it was deduced that the alkenes are not an equilibrium mixture, but are most probably formed in relative amounts determined only by the ratio of the rates at which the two types of β-hydrogen are eliminated.

The generalizations of Bailey et al. regarding the course of elimination in the pyrolysis of secondary esters have been disputed by Royals[15], and later by Eglinton and Rodger[16]. Using vapour-phase chromatography, these workers have identified both formally possible isomeric alkenes in the pyrolysates from several unsymmetrical secondary alkyl acetates, pyrolysed under conditions previously supposed by Bailey et al. to yield a single alkene. The erroneous conclusions of Bailey et al. have been attributed to failure of these workers to achieve separation of the alkenes on fractional distillation of the pyrolysates, and to their use of infrared analysis in assigning structures to the mixed (supposedly pure) olefinic products. This has been admitted by Bailey and Hale[17] in a recent publication, in which it is suggested that although exclusive Hofmann elimination does not generally occur, elimination at high temperatures (ca. 600°) may follow the Hofmann Rule preferentially, the Saytzeff Rule predominating at lower temperatures (ca. 220°). This latter conclusion has been refuted by DePuy et al.,[18]

who suggest that traces of residual acid left after cleaning the pyrolysis tube may have had a catalytic influence on the course of pyrolysis of the esters studied by Bailey et al.

The eliminations thus far discussed do not facilitate prediction of which alkene will be preferentially formed by A' scission of a particular ester when there are two possible courses of elimination. Hughes, Ingold, et al.[19] have pointed out that, although apparently antithetical, the forces motivating elimination by the Hofmann Rule and by the Saytzeff Rule may co-exist, either in conjunction or in opposition, the outcome being entirely dependant on the particular conditions for each system.

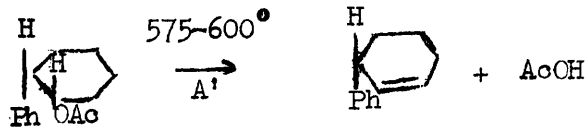
Hurd and Blunck[20] have proposed a mechanism for A' scission, involving formation of a transient 6-membered ring by bonding of the β-hydrogen atom with the carbonyl oxygen of the carboxyl group:



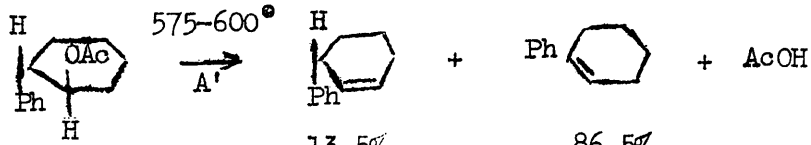
This mechanism, although criticized by Houtman et al.[10] on the basis of lack of evidence for hydrogen bonding with atoms other than strongly electronegative ones, is now widely accepted,[21] with certain qualifications. A similar mechanism has been proposed for the analogous Tschugaeff reaction,[22] which occurs on pyrolysis of alkyl xanthates. Maccoll[23] has described A' scission as a 'quasi-heterolytic', unimole-

cular reaction, in which the inductive effect of the alkyl substituents may have a strong influence on the polarity of the O and H atoms undergoing bond formation, and hence on the rate of thermal decomposition.

In 1949, Barton[24] postulated that a cis configuration of the eliminated groups in the reactant is sterically essential for A' to occur. This stereoselectivity has been strikingly demonstrated by Alexander and Mudrak,[25] who pyrolysed both cis- and trans-2-phenylcyclohexyl acetate:



92.8%



13.5% 86.5%

A similar result was observed by Arnold et al.[26] for the pyrolysis of cis- and trans-2-methylcyclohexyl acetates, and, more recently, by Wright[27], who pyrolysed the cis and trans isomers of 1-cyano-2-methylcyclohexyl acetate.

Although the above transition state theory for A' scission accounts satisfactorily for the predominance of cis pyrolytic elimination, it cannot explain the small, but detectable amount of trans product sometimes observed. Gould[28] has suggested for such examples that if there is no thermal isomerisation, either of the ester before elimination or of the product after elimination, the momentary heterolytic alkyl-oxygen scission of the ester into a pair of transient ions must

be considered as the first stage of breakdown. Molecular rotation during this brief, but significant time interval may allow another β-hydrogen atom, originally trans to the acyl group, to enter the cis position and be subsequently eliminated. According to Gould, a higher activation energy would almost certainly be required for this process than for direct elimination, so that while cis pyrolytic elimination normally predominates, trans elimination may occur to some extent at high temperatures.

1.1.3 Alkenyl-oxygen Scission (A^2)

This mode of scission, formally similar to A^1 scission of alkyl esters, has been observed as a minor, competitive route in the pyrolysis of certain α,β-alkenyl esters, yielding an acid and an alkyne as products:

$$R \cdot CO\,O\,\overset{|}{C} : \overset{|}{C}H \xrightarrow{A^2} R \cdot COOH + -C{:}C-$$

For example, A^2 scission has been observed by Allan, Forman and Ritchie[29] as a route in the pyrolysis of vinyl benzoate:

$$BzO \cdot CH : CH_2 \xrightarrow{A^2} BzOH + CH : CH$$

A^2 scission is thought to occur by an analogous mechanism to that of A^1 scission, although the A^2 reaction generally requires a higher temperature. Since a study of models indicates that the Hurd and Blunck 6-membered ring is formed with about the same ease for alkyl and alkenyl esters, the higher temperature of breakdown of alkenyl esters is possibly a reflection of the strengthening influence of the existing double bond on the breaking C-O single bond.

1.1.4 Alkynyl-oxygen Scission (A^3 : as yet unknown)

Although the pyrolysis of alkynyl esters does not appear to have been investigated, thermal breakdown analogous to the A' and A^2 scissions described above may be predicted. Thus, for example, ethynyl acetate may undergo pyrolysis to acetic acid and free carbon:

$$AcO\,C : CH \xrightarrow[?]{A^3} AcOH + 2C$$

Alternatively, decarboxylation (C^2 : see below) to methylacetylene may occur:

$$Ac\,O\,C : CH \xrightarrow[?]{C^2} CH : CMe + CO_2$$

A third possibility is acyl-oxygen scission (B' : see below) to keten (2 moles) as follows:

$$Ac\,OC : CH \xrightarrow[?]{B'} CH_2 : CO + \left[HO \cdot C : CH \rightleftharpoons CH_2 : CO\right]$$

1.1.5 Acyl-oxygen Scission (B', B^2)

Esters which cannot undergo A' scission, e.g. by lack of an available β-hydrogen atom, are relatively thermostable. Acyl-oxygen scission of such esters may occur in either of two distinct ways, designated B' scission and B^2 scission respectively.

B' scission is an acyl-oxygen scission in which an α-hydrogen atom migrates from the acyl to the alkoxy group with formation of a keten and a hydroxy compound:

$$\rangle CH \cdot CO \cdot O \cdot CH \xrightarrow{B'} \rangle C : CO + HO \cdot CH$$

The arrow indicates the direction of migration of the hydrogen atom.

Examples of esters which decompose thus are phenyl acetate[20] and vinyl acetate[28]:

$$AcOPh \xrightarrow{B'} CH_2 : CO + PhOH$$

$$AcOCH : CH_2 \xrightarrow{B'} CH_2 : CO + \left[HO \cdot CH : CH_2 \rightarrow Me \cdot CHO\right]$$

The hydroxy compound formed may be stable (e.g. phenol) or an unstable enol (e.g. of acetaldehyde).

B^2 scission, in which an α-hydrogen atom migrates from the alkoxy to the acyl group, yields two carbonyl compounds, which may be either dissimilar or identical:

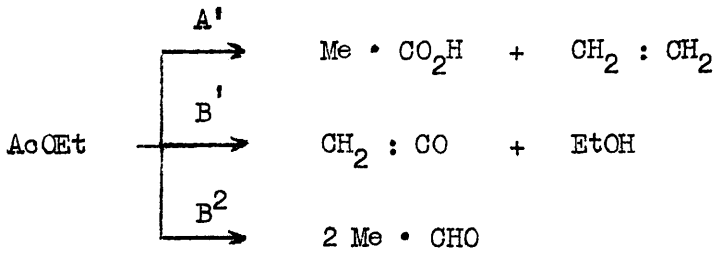
$$\text{>CH} \cdot CO - OCH\text{<} \xrightarrow{B^2} \text{>CH} \cdot CHO + O : C\text{<}$$

Thus, B^2 scission is formally a reversal of the Tishchenko reaction.[30] Methyl acetate[7] and benzyl benzoate[31] each exhibit B^2 scission on pyrolysis:

$$Me \cdot COOMe \xrightarrow{B^2} MeCHO + CH_2O$$

$$BzO \cdot CH_2Ph \xrightarrow{B^2} 2\ Ph \cdot CHO$$

B' scission is generally restricted to alkenyl and aryl esters, and B^2 to alkyl esters. The products observed by Hurd and Blunck in the pyrolysate from ethyl acetate[20] are compatible with primary, competitive B' and B^2 scissions, however, although A' is of course the main route of thermal decomposition:



Reininger and Ritchie[32] have recently measured the relative amounts of B^2 scission products in the pyrolysates from vinyl o-, m-, and p- chlorobenzoates, and found that the extent of B^2 scission decreased with increasing distance of the chlorine atom from the carboxyl group. B^2 scission has not been observed, moreover, for vinyl benzoate.[28] It was deduced that the strong, electron-attracting inductive effect of chlorine has a profound influence on the polarity of the acyl-oxygen bond undergoing scission, and a heterolytic mechanism has been proposed for the B^2 scission of the esters studied.

No mechanistic studies have yet been made of B' scission.

1.1.6 Decarbonylation (C')

The direct decarbonylation of esters is uncommon, the few examples given in the literature being confined mainly to formates. C' scission of formates may be considered analogous to the commonly-observed pyrolytic decarbonylation of aldehydes [1], since both classes of compound contain the aldehydo functional group, -CHO. Alternatively, it may be regarded as a special kind of B' scission, in which migration of the hydrogen atom to the alkoxy group leaves simply carbon monoxide:

$$H \cdot COOR \xrightarrow{C'} CO + ROH$$

For example, phenyl formate readily undergoes exclusive C' scission to phenol on distillation:[33]

$$HCOOPh \xrightarrow{C'} CO + PhOH$$

Similarly, carbon monoxide, and the small amounts of methanol and ethanol observed in the pyrolysates from methyl formate[34] and ethyl formate[3] respectively are attributable to C' scission of these esters.

Pentaerythritol tetraformate, pyrolysed at 220 - 230°, has been reported[35] to yield pentaerythritol quantitatively:

$$C(CH_2O \cdot CO \cdot H)_4 \xrightarrow{C'} C(CH_2OH)_4 + 4CO$$

Calvin and Lemmon[36] have investigated the pyrolytic decarbonylation of ethyl pyruvate and have shown it to be a true example of ester C' scission. The carbon monoxide observed in the pyrolysate from this ester would be expected to arise by elimination of the α-keto group, but by introducing the radioactive isotope ^{14}C into this group, and subsequently analysing the products of pyrolysis for radioactivity, only the non-gaseous residue was found to contain ^{14}C.

$$Me \cdot {}^{14}CO \cdot COOEt \xrightarrow{C'} CO + \text{trace } CO_2 + (\text{residue containing } {}^{14}C)$$

No acceptable general mechanism for C' scission of esters has yet been proposed.

1.1.7 Decarboxylation (C^2)

Very few examples of direct decarboxylation of esters have been reported. Phenyl maleate and phenyl fumarate have long been known to

yield phenyl cinnamate on pyrolysis, the latter undergoing secondary decarboxylation to trans-stilbene.[37]

$$\begin{matrix} CH \cdot COOPh \\ \| \\ CH \cdot COOPh \end{matrix} \xrightarrow[-CO_2]{C^2} Ph \cdot CH : CH \cdot COOPh \xrightarrow[-CO_2]{C^2} Ph \cdot CH : CHPh$$

(cis or trans) (trans)

Recent work in these laboratories has shown decarboxylation (C^2) to be a general reaction for esters which have an α,β-unsaturated acyl or alkoxy group. Thus, for example, both vinyl benzoate[28] and phenyl acrylate[38] have been observed to undergo C^2 scission:

$$BzO \cdot CH : CH_2 \xrightarrow{C^2} Ph \cdot CH : CH_2 + CO_2$$

$$CH_2 : CH \cdot COOPh \xrightarrow{C^2} Ph \cdot CH : CH_2 + CO_2$$

Vinyl acetate similarly undergoes C^2 scission to propene.[28]

$$AcOCH : CH_2 \xrightarrow{C^2} Me \cdot CH : CH_2 + CO_2$$

Of the saturated, aliphatic open-chain esters which have been pyrolysed, only formates have been reported to undergo C^2 scission. Myricyl formate, for example,[39] yields triacontane on dry-distillation:

$$H \cdot CO\ O\ C_{30}H_{61} \longrightarrow C_{30}H_{62} + CO_2$$

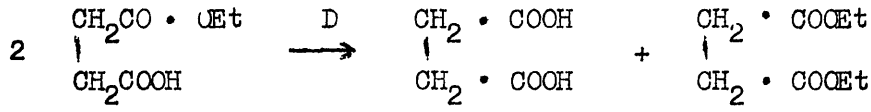
Staudinger[40] has shown that, in general, β-lactones undergo pyrolytic C^2 scission to alkenes:

$$\begin{matrix} R'R^2C - CO \\ | \quad\ | \\ R'R^2C - O \end{matrix} \xrightarrow{C^2} R'R^2C : CR'R^2$$

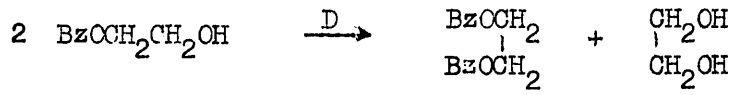
No acceptable general mechanism has yet been proposed for C^2 scission of esters.

1.1.8 Disproportionation (D)

Esters may undergo disproportionation in several ways. The well-known D reaction of monoesters of dibasic acids on pyrolysis is illustrated by the behaviour of monoethyl succinate, which yields diethyl succinate and succinic acid on dry-distillation:

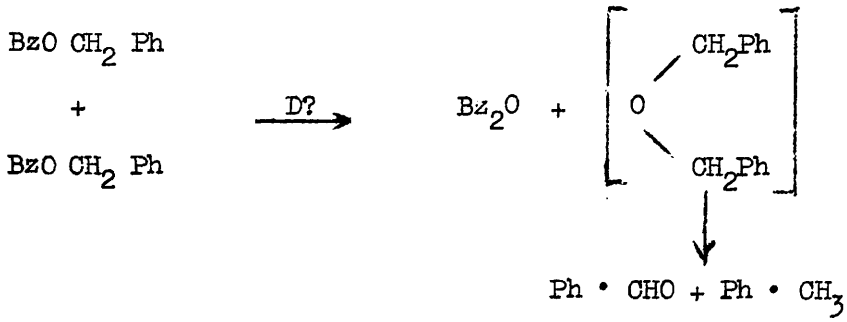


Similarly, monoaryl esters of ethylene glycol have been shown[41] to yield ethylene glycol and the corresponding diester; thus, for 2-hydroxyethyl benzoate:



A different kind of D reaction is undergone by ethylidene dibenzoate, which on pyrolysis[42] yields benzoic anhydride and acetaldehyde:

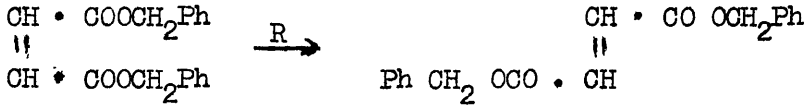
A D reaction has been proposed by Hurd and Bennett[31] to account for the presence of toluene, benzaldehyde, and benzoic anhydride in the pyrolysate from benzyl benzoate:

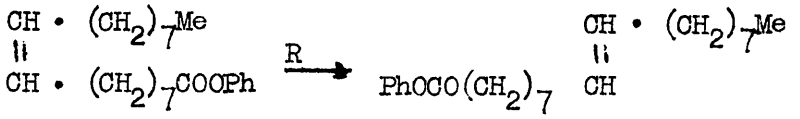


There is no obvious general mechanism for D reactions of esters, although it can be said that the usual result is an increase in molecular symmetry.

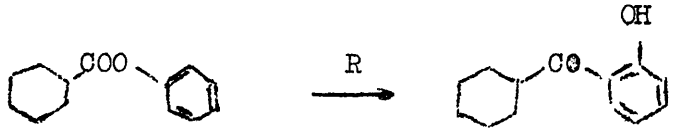
1.1.9 Rearrangement (R)

Several different kinds of thermal rearrangement of esters are known. Early examples given in the literature include the geometrical isomerisation of dibenzyl maleate to dibenzyl fumarate[43], and of phenyl oleate to phenyl elaidate.[44]

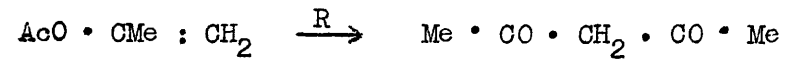




Another kind of rearrangement (R) is the pyrolytic conversion of phenyl cyclohexanecarboxylate to cyclohexyl o-hydroxyphenyl ketone.[45]



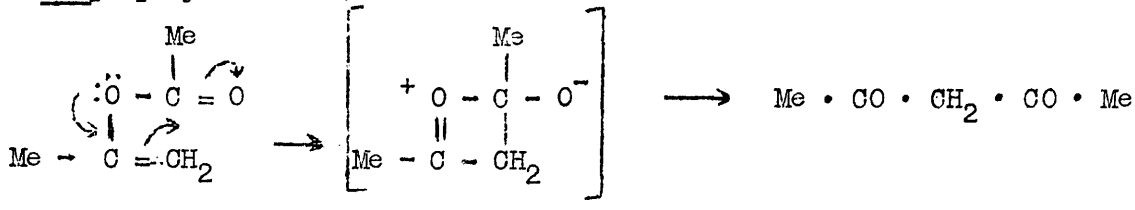
The rearrangement (R) of enol carboxylates (other than vinyl esters) to β-diketones has been demonstrated by Young et al.[46] This reaction is now known to be reversible, the equilibrium strongly favouring formation of the β-diketone at ca. 500°.[47] Thus, isopropenyl acetate undergoes rearrangement to acetylacetone:



Allan and Ritchie[48] have observed the analogous rearrangement (R) of cyclohex-1-enyl benzoate to 2-benzoylcyclohexanone, and Allan, Forman and Ritchie[28] postulate rearrangement of vinyl carboxylates to β-ketoaldehydes, which, being unstable, were not isolated, but probably undergo decarbonylation to the appropriate ketones observed with carbon monoxide in the pyrolysate. The acetophenone observed in the pyrolysate from vinyl benzoate is explained thus:

$$Ph \cdot CO\,OCH : CH_2 \xrightarrow{R} \left[Ph \cdot CO \cdot CH_2 \cdot CHO\right] \downarrow \; Ph \cdot CO \cdot CH_3 + CO$$

Young et al.[46] have suggested that this kind of rearrangement occurs by intramolecular formation of a 4-centre cyclic transition state, e.g. for isopropenyl acetate:



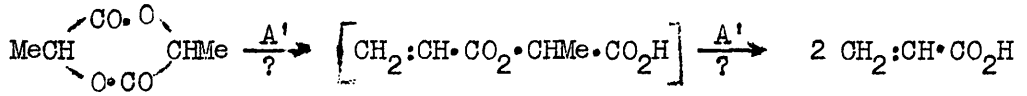
1.2 The Pyrolysis of Lactides and other Derivatives of α-Hydroxy Acids

During a search for a new general synthetic route to polymerisable monomers of the acrylic acid type, it was shown by Burns, Jones and Ritchie[49] that methyl lactate can be smoothly but indirectly converted to methyl acrylate by vapour-phase pyrolysis of methyl α-acetoxypropionate at ca. 480°, thus:

$$MeCH(OH)CO_2Me \longrightarrow MeCH(OAc)CO_2Me \xrightarrow[480^\circ]{\Delta} AcOH + CH_2 : CH \cdot CO_2Me$$

It might therefore be predicted, a priori, that lactide (I), containing

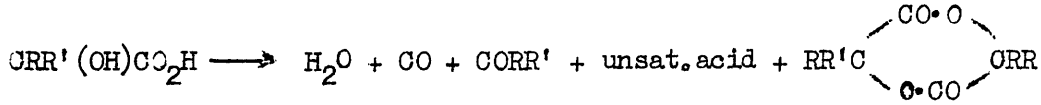
two ester groupings each with an available β-hydrogen, would break down pyrolytically in an analogous way, yielding acrylic acid, perhaps in two stages, thus:



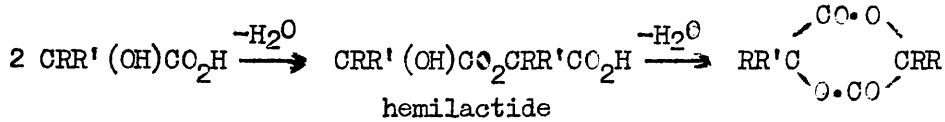
(I)

It had, however, been noted previously by Blaise[50] that (I) pyrolyses to acetaldehyde and carbon monoxide. There is no immediately obvious reason for elimination of carbon monoxide in this way, and before considering possible mechanisms, it is desirable to review the known pyrolytic decompositions of the other groups of related substances which also yield carbon monoxide - (a) α-hydroxy acids, and (b) α-acyloxy acids.

(a) Blaise and Bagard[51] have shown that, in general, the products obtained on dry-distillation of a given α-hydroxy acid are water, carbon monoxide, a carbonyl compound, an α, β-unsaturated acid and the corresponding lactide:

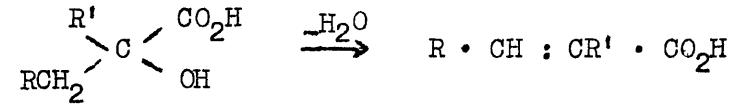


The formation of the lactide and of the α, β-unsaturated acid are competitive modes of elimination of water, the former being a two-stage intermolecular esterification with intermediate formation of a hemi-lactide:



hemilactide

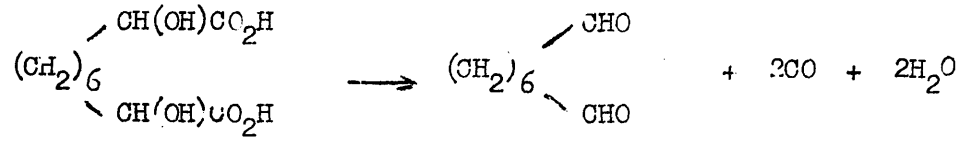
and the latter a simple intramolecular elimination of water, thus:



A mixture of isomeric α,β-unsaturated acids may, of course, be formed from an α-hydroxy acid containing a dissymmetrically disubstituted α-carbon atom.

The ratio of the products observed on pyrolysis of an α-hydroxy acid varies markedly with the size of the α-substituent(s). For instance, the formation of α,β-unsaturated acids appears to be favoured by large alkyl α-substituents, whereas α-hydroxy acids of low molecular weight form lactides in yields which may be as high as 30%. The yields of such lactides fall off rapidly with increasing molecular weight, however, so that in the α,α-disubstituted series, for example, no lactides have been reported for diethylglycollic acid or higher homologues.

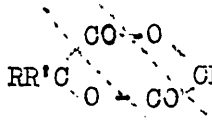
The occurrence of a carbonyl compound and carbon monoxide as major products of pyrolysis is not readily explained. The carbonyl compound formed may be an aldehyde (for a mono-substituted α-carbon atom) or a ketone (for a disubstituted α-carbon atom). Le Sueur[52] has observed analogous results for certain α,α' dihydroxy dibasic acids. For example:



Following the report by Blaise[50] that many aliphatic aldehydes could be obtained in good yields (50 - 60%) by dry-distillation of the

appropriate lactides, Bagard[53] recorded that on pyrolysis of α - hydroxyheptoic acid he obtained a 50% yield of caproic aldehyde, and that by arresting pyrolysis at an early stage, he isolated heptolactide among other minor products. Subsequent pyrolysis of this lactide at 280° - 300° yielded caproic aldehyde.

It has been tentatively suggested by Hurd[1] on the basis of the above results, that "it is reasonable to infer that loss of carbon monoxide (from α-hydroxy acids) is more properly a function of the lactide than of the α-hydroxy acid". Hurd, however, offers no detailed mechanism for the elimination of carbon monoxide from the lactide, which may be represented in general thus:



$$RR'C(CO{\cdot}O)_2CRR' \longrightarrow 2\ CORR' + 2\ CO$$

(b) It was first shown by Bagard[53] that α-acyloxy acids break down thermally as follows:

$$R \cdot CO_2CH\ R'\ CO_2\ H \longrightarrow R \cdot CO_2H + R'CHO + CO$$

This is in sharp contrast to the pyrolytic behaviour of the corresponding α-acyloxy methyl esters, which, as shown by the example given above, yield the expected α, β-unsaturated methyl ester by A' scission. An analogous result was recorded by Le Sueur[52] for the α, α'-diacyl derivatives of α, α'-dihydroxy dibasic acids; thus, for example:

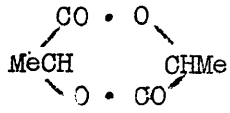
$$(CH_2)_6\begin{matrix}CH(OAc)CO_2H\\CH(OAc)CO_2H\end{matrix} \longrightarrow (CH_2)_6\begin{matrix}CHO\\CHO\end{matrix} + 2\ AcOH + 2\ CO$$

The aldehydes formed on pyrolysis of an α-acyloxy acid contains one carbon atom less than the parent α-hydroxy acid, this being one of the classical descents of a homologous series.

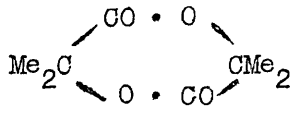
1.3 Objects of Research

No explanation has hitherto been offered for the somewhat anomalous pyrolytic behaviour of lactides and of α-acyloxy acids. The work described in Part I of this thesis deals with a more detailed investigation of their respective thermal decompositions than was possible at the time of the earlier work by Blaise, Begard et al. This closer study has been facilitated by the relatively recent advent of highly sensitive analytical techniques, such as vapour-phase chromatography and paper chromatography.

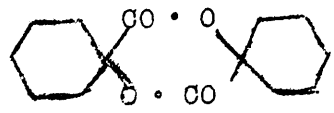
A series of three lactides was selected as being representative of the various structures encountered in that class of compounds. These are lactide (I), the lactide (II), and the spirodilactone (III):



(I)

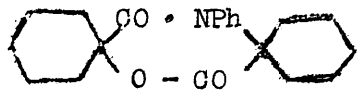


(II)



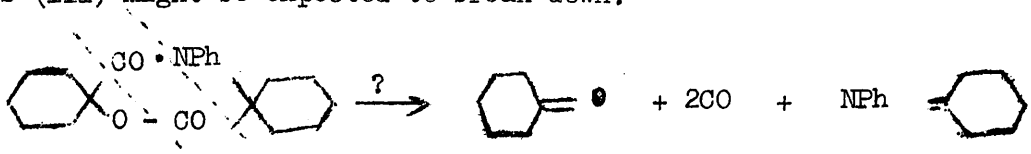
(III)

(III) was also chosen because of its structural similarity to the spiro-lactone-lactam,



which was found by Bain and Ritchie[54] to yield, on pyrolysis at ca. 540° in the vapour phase, a large gaseous pyrolysate consisting of carbon

monoxide and carbon dioxide. The formation of carbon monoxide could not be explained by assuming cleavage of the spiro-lactone-lactam just as (III) might be expected to break down:



since neither cyclohexanone not its anil could be detected in the pyrolysate.

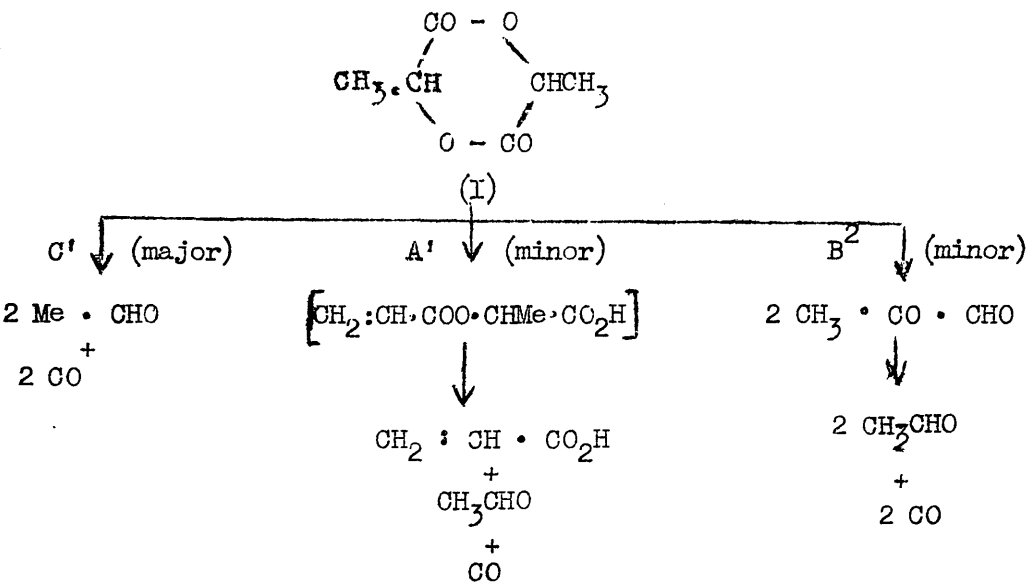
α-Acetoxypropionic acid, a typical α-acyloxy acid, was chosen to represent that class of compounds for pyrolysis studies in the present work.

2. DISCUSSION OF RESULTS

2.1 Pyrolysis of (I)

At 500° in a Pyrex glass flow reactor, (I) decomposes to the extent of ca. 50% (Runs 1 and 2) yielding, as is predictable from the work of Blaise[50] acetaldehyde and carbon monoxide as major products. In addition, however, ethylene and carbon dioxide were observed as minor products, together with traces of methylglyoxal and acrylic acid; this shows the thermal breakdown of (I) to be more complex than was formerly believed. Other substances sought, (see below) but with negative results, were acraldehyde, pyruvic acid, ethyl acrylate, α-acetoxypropionaldehyde, 2-methylbut-3-enoic acid, but-1-ene and but-2-ene.

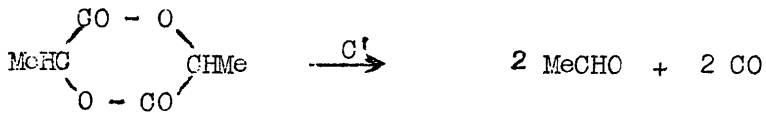
The best interpretation of the results indicates decomposition of (I) by three competitive routes, as follows:



Major C' scission of (I)

Carbon monoxide is the secondary product of pyrolysis by both the A' and B^2 routes, as indicated in the annexed scheme. Pyrolysis by the A' route should result in formation of acrylic acid, acetaldehyde and carbon monoxide in equimolar amounts. In view of the extremely small ratio of acrylic acid to carbon monoxide observed (Runs 1 and 2), however, this route can make only a very small contribution to the total quantity of carbon monoxide observed. Pyrolysis by the B^2 route should result in the formation of equal quantities of acetaldehyde and carbon monoxide. Although a separate semi-micro pyrolysis of the intermediate, methylglyoxal (Run 14) confirms this route qualitatively, the decomposition of methylglyoxal occurred only to the extent of ca. 50%. From the trace amount of methylglyoxal observed in the pyrolysate from (I), it is concluded that the B^2 route can only make a minor contribution to the carbon monoxide observed on pyrolysis of (I).

The only plausible explanation of the large amount of carbon monoxide from (I) is therefore that it is formed mainly by direct C' scission of (I) to acetaldehyde (formed in roughly equimolar amount to the carbon monoxide).



Minor Alkyl-Oxygen Scission (A') of (I)

Alkyl-oxygen scission (A') is shown to take part in the pyrolysis of (I) by the positive test for a carboxylic acid given by the main

pyrolysate (Runs I and II) before fractionation. Although the acid formed could not be detected in any of the various fractions obtained in distillation of the main pyrolysate, the addition of hydroquinone to the pyrolsand (Run 8) resulted in the identification of acrylic acid as a minor product.

Since alkyl-oxygen scission (A') is normally the major route of pyrolytic decomposition of esters possessing an available β-hydrogen, it might have been predicted that (I) would break down thus, by a double A' scission yielding acrylic acid as a major product. In accounting for the observed deficiency of acrylic acid, two possibilities may be considered:

(a) its secondary thermal breakdown during pyrolysis

and (b) its polymerisation during fractionation.

(a) It has been shown by Mackinnon[55] that acrylic acid breaks down on pyrolysis at ca. 500°, under comparable conditions, to the extent of ca. 25% yielding mainly carbon dioxide and ethylene. The quantities of carbon dioxide and ethylene observed in the gaseous pyrolysate from (I), however, were not equimolar, there being a large excess of carbon dioxide. Ethylene, moreover, should be stable[56] under the experimental conditions employed.

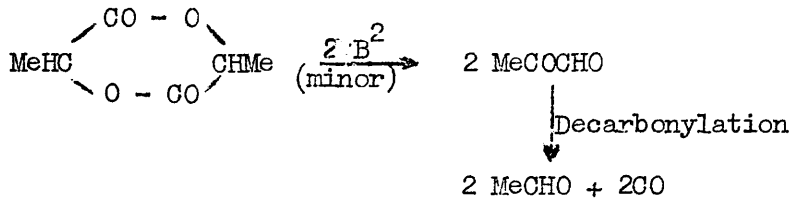
From these considerations, it may be deduced that the thermal breakdown of acrylic acid can only account for a small part of its deficiency from the pyrolysate from (I). This has been confirmed by a control experiment (Run 11) in which acrylic acid, intentionally added to the pyrolysand (I), was not completely destroyed under comparable conditions.

(b) Polymerisation of acrylic acid during fractionation of the main pyrolysate appears to be the main cause of its apparent deficiency. Supporting evidence for this argument is provided by the fact that fractionation of the pyrolysate in the presence of the polymerisation-inhibitor hydroquinone afforded a detectable amount (under 1%) of acrylic acid.

The pyrolytic formation of acrylic acid from (I) is believed to occur, not by a double A' scission route, but via a single A' scission to α-acrylyloxypropionic acid. This intermediate, although not identified (its isolation has not hitherto been reported) is an α-acyloxy acid, and is therefore likely to ne unstable at 500°, pyrolysing to acrylic acid, acetaldehyde and carbon monoxide (see above scheme).

Minor B^2 scission of (I)

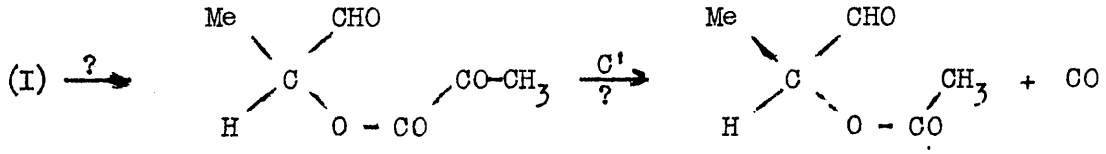
Formation of methylglyoxal from (I) is best explained by a double B^2 scission, as follows, with subsequent decarbonylation to acetaldehyde, as has been



confirmed by a separate semimicropyrolysis (Run 14) of methylglyoxal.

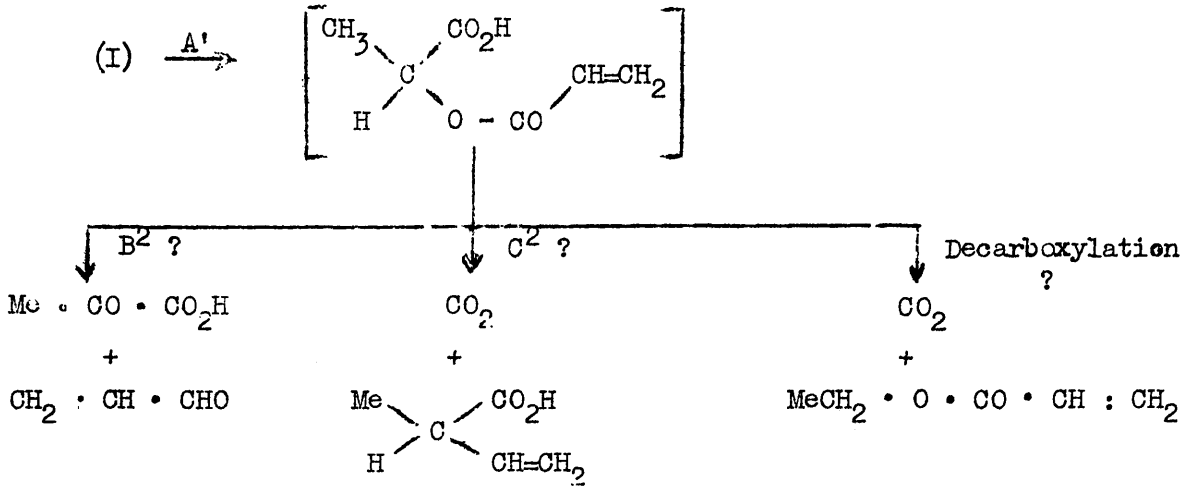
Whether methylglyoxal is formed in one stage, or in two (via lactaldehyde pyruvate) cannot be resolved with certainty, since the intermediate could not be detected; not has it been reported in the literature. In view of the known thermal instability of ethyl pyruvate[36]

partial decarbonylation (C') of lactaldehyde pyruvate to α-acetoxypropionaldehyde might have been expected, but the latter could not be detected:



Other Possible Breakdown Routes of (I)

Following a single A' scission, there are several other predictable breakdown routes as set out in the following scheme:



An A'/B^2 sequence would lead to formation of pyruvic acid and acraldehyde, neither of which could, however, be detected.

An A'/C^2 sequence would yield 2-methylbut-3-enoic acid which could not be detected (nor could its possible decarboxylation product, but-1-ene, be detected).

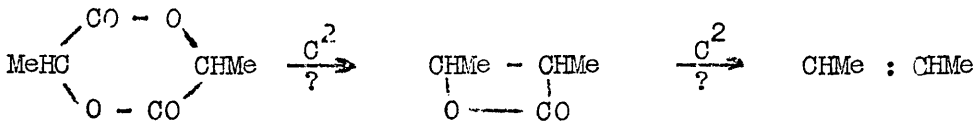
The primary A' scission product, α-acrylyloxypropionic acid, might conceivably undergo decarboxylation to ethyl acrylate (also not detected). It is known[55] that ethyl acrylate breaks down at 500° to the extent

of ca. 95%, yielding mainly its A' products acrylic acid and ethylene, and also as minor products, carbon dioxide and but-1-ene. There is nevertheless insufficient evidence to establish ethyl acrylate as an intermediate in the pyrolysis of (I).

Origin of Carbon Dioxide

The formation of all of the carbon dioxide in the pyrolysate from (I) cannot be positively attributed to any single route so far discussed, so that the possibility of a minor primary decarboxylation (C^2) of (I) must now be considered.

Primary C^2 scission of (I) would probably first yield a β-lactone, which, in accordance with the known thermal behaviour of such substances,[40] would be expected to undergo readily further decarboxylation (C^2) to but-2-ene:



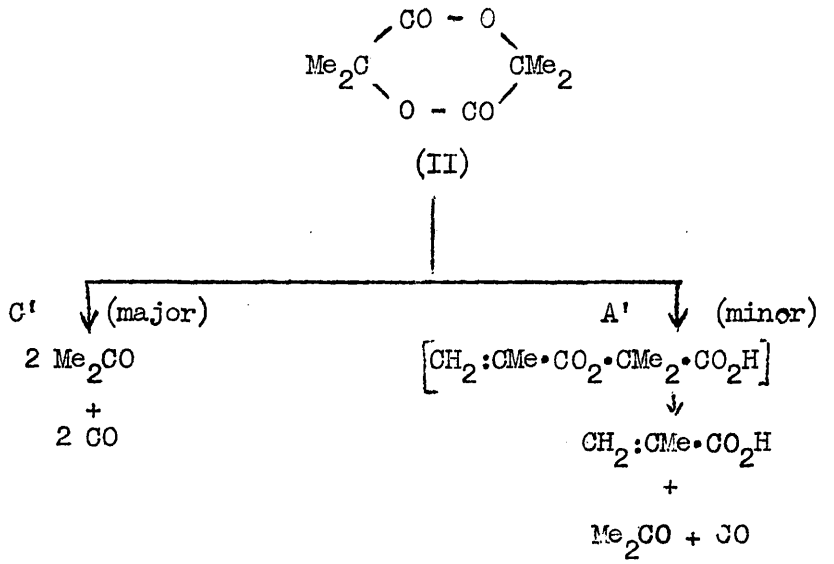
No but-2-ene could be detected, however, so that there is no experimental evidence to justify postulation of primary C^2 scission of (I). Most of the carbon dioxide in the pyrolysate from (I) therefore remains for the present unaccounted for.

2.2 Pyrolysis of (II)

(II) decomposes to the extent of ca. 69% when pyrolysed at 500° in the gaseous phase (Runs 3 and 4) yielding mainly acetone and carbon monoxide. Minor amounts of α-methylacrylic acid, propene and carbon dioxide are also formed. Other substances sought (see below) but with

negative results, were α-methylacraldehyde, 2:3-dimethylbut-2-ene, 2:3-dimethylbut-1-ene and isopropyl α-methylacrylate.

The best interpretation of the results indicates breakdown of (II) as shown in the following scheme, accompanied by certain other simple, predictable decompositions:



Alkyl-oxygen scission(A') occurs to a much greater extent in the pyrolysis of (II) than in that of (I), although it is still a minor route. Primary acyl-oxygen scission (B^2) of (II) is precluded by the absence of an available α-hydrogen atom. Possibly the only explanation other than direct C' scission that might be submitted for the formation of carbon monoxide and acetone as major products would be a primary A' scission to α-(α-methylacrylyloxy) isobutyric acid and subsequent decarboxylation of the latter to isopropyl α-methylacrylate. The isopropyl α-methylacrylate thus formed could then conceivably undergo B^2 scission to acetone and α-methylacraldehyde:

$$(II) \xrightarrow[?]{A'} \left[CH_2 : CMe \cdot CO_2CMe_2 \cdot CO_2H\right] \xrightarrow[?]{-CO_2} \left[CH_2 : CMe \cdot CO_2 \cdot CHMe_2\right]$$

$$\downarrow B^2 \; ?$$

$$CH_2{:}CMe{\cdot}CHO + Me_2CO$$

$$\downarrow$$

$$CO + CH_2 : CHMe$$

α-Methylacraldehyde is known[57] to undergo major decarbonylation to propene under comparable conditions, but although the propene and carbon monoxide thus formed should be in equimolar amounts, the gaseous pyrolysate from (II) (Runs 3 and 4) shows a great preponderance of carbon monoxide.

To test the above hypothesis, isopropyl α-methylacrylate was pyrolysed at 500° (Runs 5 and 6), yielding mainly α-methylacrylic acid and propene by A' scission,

$$CH_2 : CMe \cdot CO_2 CHMe_2 \xrightarrow{A'} CH_2 : CMe \cdot CO_2H + CH_2 : CHMe$$

and a minor quantity of acetone, accountable for as the secondary decarboxylation product of α-methylacrylic acid.[57] No α-methylacraldehyde could be detected, although 21% was found to survive pyrolysis when this was pyrolysed alone[57] at 500°.

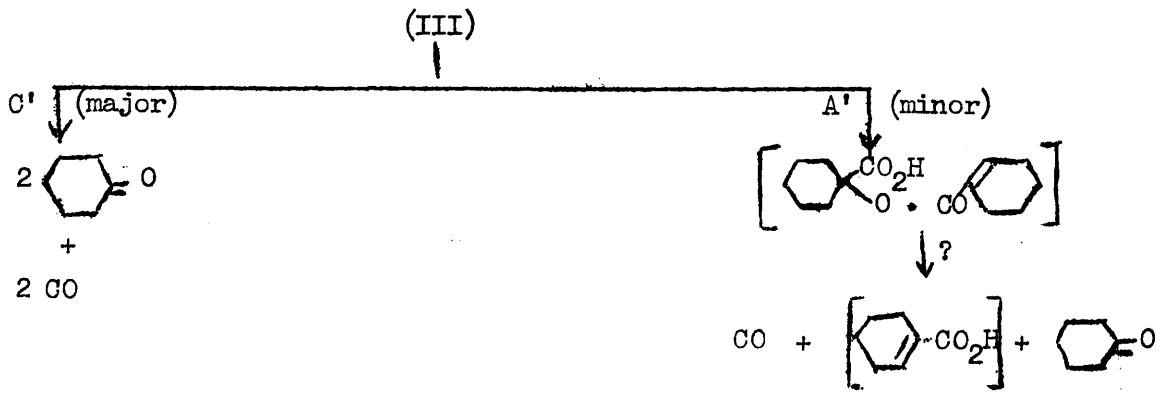
The indirect explanation outlined above must therefore be rejected in favour of direct C' scission of (II) as in the annexed scheme. The formation of α-methylacrylic acid from (II) is analogous to that of acrylic acid from (I) and requires no further comment. By a course of reasoning analogous to that employed for (I), primary decarboxylation (C^2) of (II) is excluded, since 2:3 -dimethylbut-2-ene could not be detected. Carbon dioxide and propene are qualitatively accounted for as the secondary decarboxylation products of α-methylacrylic acid.[57]

Quantitatively, however, these were not equimolar in the gaseous pyrolysate from (II); the excess of carbon dioxide remains to be accounted for. A formally possible source, which has not so far been considered, is decarboxylation (C^2) of α-(α-methylacrylyloxy) isobutyric acid to 2:2:3-trimethylbut-3-enoic acid. This acid has not hitherto been reported, and so could not be identified; its possible decarboxylation product, 2:3-dimethylbut-1-ene, could not be detected in the gaseous pyrolysate from (II), so that there is no real evidence to establish decarboxylation in this way:

$$(II) \xrightarrow{A'} \left[CH_2{:}CMe{\cdot}CO_2{\cdot}CMe_2{\cdot}CO_2H\right] \xrightarrow[?]{C^2} \left[CH_2{:}CMe{\cdot}CMe_2{\cdot}CO_2H\right] \xrightarrow[?]{-CO_2} \left[CH_2{:}CMe{\cdot}CHMe_2\right]$$

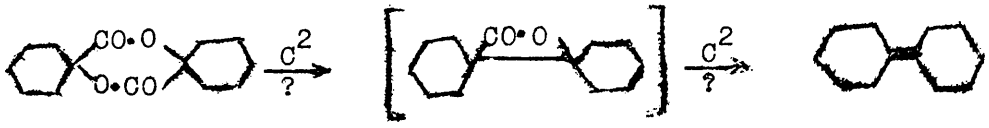
2.3 Pyrolysis of (III)

When pyrolysed at ca. 500° in the vapour phase (Runs 7 and 15), (III) decomposes to the extent of ca. 44%. As for its analogues (I) and (II), a major decarbonylation (C') appears to be the main route, yielding cyclohexanone as expected. A minor quantity of carbon dioxide was also observed. As for (II), B^2 scission is precluded by the absence of an available α-hydrogen atom. The trace amount of an unidentified carboxylic acid detected in the main pyrolysate from (III) is best explained by postulating a primary minor A' scission to the predictable α-acyloxy acid (which has not hitherto been reported). In accordance with the general pyrolytic behaviour of such acids, however, its immediate and complete breakdown to cyclohex-1-enecarboxylic acid, cyclohexanone and carbon monoxide would be expected. The annexed scheme summarizes these reactions:

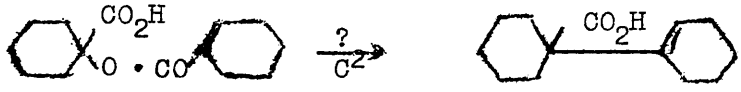


The non-detection of cyclohex-1-enecarboxylic acid (and formation of minor amounts of carbon dioxide) might be formally attributable to its further decarboxylation to cyclohexene, but, since the latter could not be detected, there is no real evidence for this.

Primary decarboxylation (C^2) of (III) must be excluded as a route, since no cyclohexylidenecyclohexane could be detected:



Similarly, there is no evidence for decarboxylation (C^2) of the primary A' product, since 1-(cyclohex-1'-enyl)cyclohexanecarboxylic acid could not be identified - it does not appear to have been recorded in the literature.



2.4 Pyrolysis of α-acetoxypropionic acid

When α-acetoxypropionic acid is pyrolysed in the vapour phase at

ca. 500° (Runs 12 and 13) it breaks down completely (ca. 100%) to give acetic acid, acetaldehyde, and carbon monoxide as the only primary products:

$$Me \cdot CO_2 \cdot CHMe \cdot CO_2H \longrightarrow Me \cdot CO_2H + Me \cdot CHO + CO$$

This result is in qualitative agreement with the earlier experimental observations of Bagard[53], for pyrolysis at lower temperatures. The traces of acetic anhydride and water detected in the main pyrolysate are readily accounted for as the secondary decomposition products of acetic acid. The A' scission product that might formally have been expected, acrylic acid, could not be detected. It had been considered formally possible that lactide (I) might be formed as an intermediate by ester-interchange, and that its subsequent breakdown might account for the formation of carbon monoxide and acetaldehyde:

$$2\ Me \cdot CO_2 \cdot CHMe \cdot CO_2H \xrightarrow{?} (I) + 2\ AcOH$$

$$(I) \xrightarrow{?} 2MeCHO + 2CO$$

No lactide (I) could be detected, however, in the pyrolysate from α-acetoxypropionic acid, so that the possibility of breakdown in this way must be rejected.

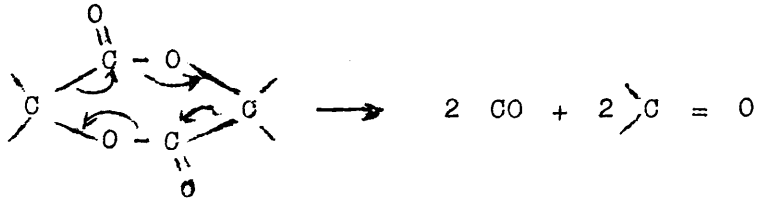
The observed complete thermal breakdown of α-acetoxypropionic acid at ca. 500° confirms an earlier report[49] that, above 450°, ethyl α-acetoxypropionate pyrolyses to α-acetoxypropionic acid. The latter, although not itself identified, was considered to be the precursor of the acetaldehyde found in the pyrolysate. The non-detection of α-acetoxypropionic acid can thus be accounted for.

2.5 Reaction Mechanisms

2.5.1 Major Decarbonylation (C') of Lactides

The major direct decarbonylation (C') of the three lactides studied is a new addition to the few examples of primary C' of esters which have hitherto been recorded.

The reaction cannot be considered to be completely free-radical in character, since it was not completely suppressed by the addition of 1% of hydroquinone (c.f. the total suppression of the intra-acyl scission (IA) of phenyl acrylate by added hydroquinone.[38]) Each of the lactides was pyrolysed, as before, in a flow reactor at 500°, in presence of the inhibitor (Runs 8, 9, 10). The pyrolysis of (I) appears to be the least affected, by comparison of the results of Runs 1 and 2 with those of Run 8, in all of which breakdown occurs to the extent of ca. 50%. Presence of the inhibitor appears to have reduced the extent of breakdown of (II) from 69% to 53%, and of (III) from 44% to 28%. Nevertheless the gas analyses in all of these runs are not much affected. It is possible to conclude from these results that the breakdown of lactides is partially free radical in character, but, to give them any real significance, a long series of pyrolyses would have to be done, with and without added hydroquinone, and the results analysed by statistical methods. For the present, the decarbonylation is considered to occur mainly by a concerted rearrangement of electrons as shown, resulting in formation of the experimentally observed products

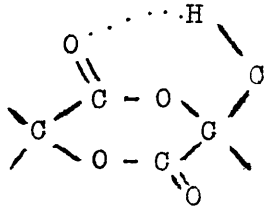


This simple mechanism which requires no migration of atoms or groups, should be favoured by the Principle of Least Motion,[7] according to which a reaction involving the minimum molecular deformation of the reactant(s) is favoured.

2.5.2 Minor Alkyl-oxygen Scission (A') of Lactides

An outstanding feature of the pyrolysis of all three lactides studied is the minor rôle of alkyl-oxygen scission (A'), which is almost invariably the predominating route of breakdown of simple esters possessing an available β-hydrogen in the alkyl group.

The only plausible explanation for its suppression is that the steric requirements of the A' scission mechanism first postulated by Hurd and Blunck[20] are not fulfilled. Formation of the quasi-6-membered ring required by this theory necessarily involves close proximity of an exocyclic β-hydrogen atom with the carbonyl oxygen of an ester linkage as shown:



This arrangement would apparently place too much internal strain on the lactide molecule, which would account for the observed minor rôle of alkyl-oxygen scission. Manipulation of Stuart models for (I) - (III) supports this conclusion. A β-hydrogen atom can just be made to touch the corresponding carbonyl oxygen atom, but considerable strain is thus placed upon the bonds joining the atoms in the lactide ring. In none

of the three models (I)-(III), moreover, was it possible to achieve the arrangement necessary for a double, simultaneous A' scission of the lactide, which is therefore considered unlikely. Although lactide (I) can exist in a trans form (with methyl groups above and below the plane of the ring) and two enantiomorphic cis forms (with both methyl groups on one side of the ring) the models for these forms all exhibit similar A' behaviour.

Statistically, the expected order of decreasing extent of A' scission (based solely on the number of available β-hydrogen atoms) would be (II), (III), and (I), which have 12, 8, and 6 β-hydrogen atoms respectively. The order observed experimentally, however, was (II), (I), and (III). The abnormally low yield of A' scission product from (III) is probably best explained by the fact that, in the Stuart model, all four valency bonds of each spiro carbon atom are held rigidly in space, and do not readily permit approach of a β-hydrogen atom to the corresponding carbonyl oxygen atom without rupture of the C - C bonds of the molecule.

Similar results were observed by Bird[58], who, in an independent investigation, found that both γ-butyrolactone and δ-valerolactone are thermostable at ca. 590°, and do not break down by alkyl-oxygen scission (A') to the corresponding terminally unsaturated acids. It was found, moreover, that ϵ-caprolactone yielded 5% of unsaturated acid at ca. 520° and 52.8% at ca. 580°, while ϵ-methyl ϵ-caprolactone is smoothly converted pyrolytically at these temperatures to unsaturated acid by A' scission involving a β-hydrogen atom of the exocyclic methyl group.

Straight chain lactones of larger ring-size were found to be readily converted thermally to the corresponding unsaturated acids. It was deduced that only in the larger rings is there sufficient flexibility to allow mutual interaction between the β-hydrogen and carbonyl oxygen atoms. Although Bird did not study the pyrolysis of δ-valerolactone or its analogue δ-methyl δ-valerolactone, it is apparent from his work that the minimum ring-size n necessary to permit ready A' scission of straight chain lactones is approximately n = 8 (where n is the number of atoms in the ring), or n = 7 if an ω-methyl group is also present in the molecule.

Huisgen and Ott[59] have observed that, in a series of ω-lactones, the physical constants (e.g. boiling points, dipole moments, and rate constants of alkaline hydrolysis) fall into two groups, corresponding to cis and trans configurations about the single C - O bond of the ester group. The ring structure of the lactones of ring size n = 4 to 7 forces these into the energetically less favoured cis configuration, whereas the larger lactones, of n = 10 to 16, assume the energetically more favourable trans configuration, a planer conformation inherent in simple, open-chain esters. Lactones of n=8 and 9 were found to be intermediate in character.

To correlate these two sets of observations, the present author constructed Stuart models of lactones of about the critical ring-size, n = 8. It was found that formation of the quasi-6-membered ring required for A' scission was most readily accomplished when the lactone model was manipulated into the trans configuration. The observations of Bird and

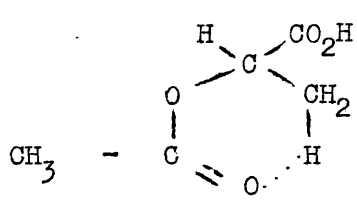
of Huisgen and Ott are thus found to be in good agreement.

Applying these observations to the present investigation, it is clear that lactides fall into the category of double cis esters. This explains their reluctance to undergo A' scission. In the investigation of the pyrolysis of lactones, Bird did not observe any decarbonylation (C'), although this has been found to be the major route of pyrolysis for lactides. This anomaly may be explained by the concerted mechanism postulated above for the C' of lactides. Lactones, having only a single carboxyl group, are structurally incompatible with decomposition by such a mechanism, and C' has not been reported, moreover, for simple, open-chain esters. Since the cis ester configuration has an excess of free energy of ca. 3.6 K cal./mole over the trans[59] the energy of activation for decarbonylation of each lactide molecule should therefore be compensated by ca. 7.2 K cal, and the reaction thus facilitated.

2.5.3 Mechanism of Thermal Breakdown of α-acyloxy acids

The absence of A' scission from the pyrolysis at 500° of α-acetoxypropionic acid is remarkable in that there is no immediately obvious structural feature that could preclude formation of the quasi-6-membered ring required for A' by the Hurd and Blunck mechanism.

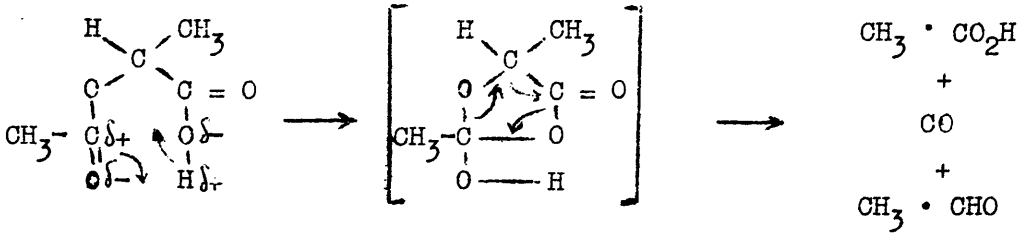
Manipulation of the Stuart model for α-acetoxypropionic acid confirms this: proximity of a β-hydrogen atom to the carbonyl oxygen of the acetoxy group is readily achieved:



Similar ease of formation of a quasi-6-membered ring is encountered with methyl α-acetoxypropionate, as expected. Maccoll[23] has established that for simple esters, the Hurd and Blunck mechanism is more properly "quasi-heterolytic", depending for its ease of occurrence on the inductive effect of the alkyl substituents (if any) on the α-carbon atom, and their corresponding influence on the polarity of the O and H atoms undergoing bond formation in the transition state.

Since the carboxylic acid group and carbomethoxy group are similar in their electron-attracting inductive effect, it is considered unlikely that any such difference could cause the wide variation observed in the thermal behaviour of the compounds under discussion. The observed mode of thermal decomposition of α-acetoxypropionic acid is therefore most probably facilitated by the achievement of some preferred configuration involving a special feature of the carboxylic acid group not possessed by the carbomethoxy group; an obvious such feature is the high mobility of the carboxylic proton.

Formation of the quasi-6-membered ring of A' scission theory requires, in the last analysis, some form of hydrogen bonding. The forces involved should therefore be weak. The mechanism which is now proposed for the observed breakdown of α-acetoxypropionic acid is in effect a concerted mechanism activated by relatively strong electrostatic forces, as shown in the following simplified scheme:

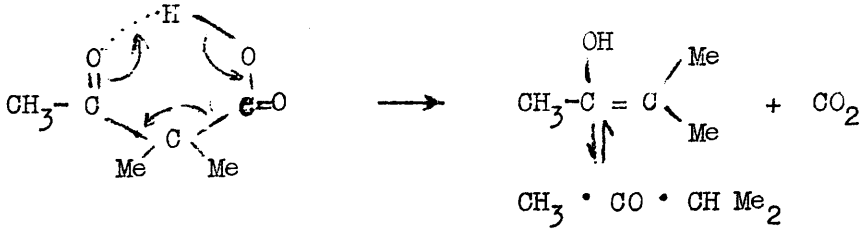


The ester carbonyl group, like the carbonyl group of ketones, is normally slightly polarized as shown (as witness the addition reaction with Grignard reagents exhibited by both classes of compound). The carboxylic acid group is even more highly polarized, of course, and, as a result of electrostatic attraction between the two groups, formation of the transient intermediate is thought to occur.

Although this does not occur at lower temperatures (α-acetoxypropionic acid distils without decomposition at 127°/11 mm.), migration of the proton is thought to be facilitated energetically at the more elevated temperatures of pyrolysis.

The transient intermediate postulated should be sterically strain-free, since it is readily formed by Stuart models. Breakdown of the intermediate is thought to occur by the concerted mechanism shown, which involves no migration of atoms or groups, and results in formation of the experimentally observed products.

A somewhat similar reaction mechanism has been proposed by Westheimer and Jones[60], for the decarboxylation of the β-keto acid intermediate formed in the acid-catalysed 'ketone hydrolysis' of β-keto esters. It was proposed that decarboxylation of the undissociated β-keto acid occurs <u>via</u> a 6-membered cyclic transition state, formed by mutual interaction between the carboxylic proton and the oxygen atom of the β-carbonyl group; thus for dimethylacetoacetic acid:



2.6 Conclusions

The individual results of pyrolysis of lactides and related substances have been discussed above as fully as possible; the overall significance of these results is considered below.

The minor rôle of primary A' scission in the pyrolytic breakdown patterns of lactides and of α-acyloxy acids arises from the intervention of steric and electrostatic factors respectively, which avert the normal course of predominant A' scission. In the pyrolysis of lactides, primary A' scission is sterically hindered by difficulty of formation of the quasi-heterolytic 6-membered ring required by the Hurd and Blunck theory, an effect particularly marked in the pyrolysis of the spiro-dilactone (III), which, as shown by a study of models, exhibits high molecular rigidity. The absence of A' scission from the pyrolytic breakdown of α-acyloxy acids is attributed to the intervention of intramolecular electrostatic forces, which enable preferential formation of a transient 5-membered cyclic intermediate to occur.

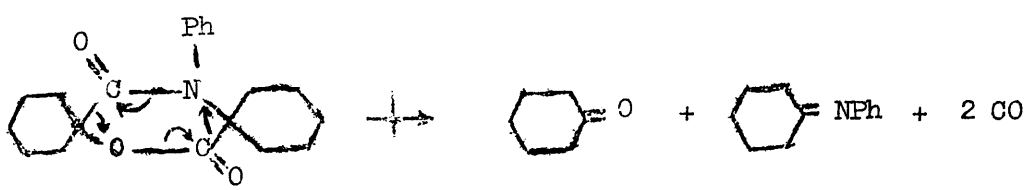
The observed major routes of pyrolytic decomposition of lactides and of α-acyloxy acids are attributed to breakdown by concerted mechanisms which, involving no migration of atoms or groups, are favourable according to the Principle of Least Motion.

Lactides in general break down mainly by direct decarbonylation (C') to a carbonyl compound, as is predictable from the earlier work of Blaise, Bagard et al., but evidence for a minor, primary A' scission (and subsequent secondary reactions) is usually also observed.

Lactide (I), possessing available α-hydrogen atoms, also exhibits, in addition to the above breakdown reactions, a minor double B^2 scission to methylglyoxal, which undergoes partial secondary decarbonylation to acetaldehyde.

α-acyloxy acids appear to break down completely to give as the only primary products carbon monoxide, a carboxylic acid, and a carbonyl compound containing one carbon atom less than the parent α-hydroxy acid.

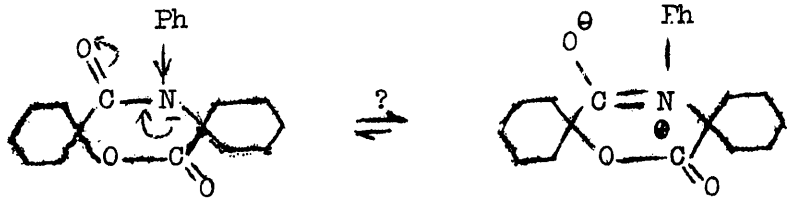
The concerted general mechanism which has been proposed for the thermal decomposition of lactides cannot be applied to explain the formation of carbon monoxide as a product of pyrolysis of the spiro-lactone-lactam studied by Bain and Ritchie[54], since an analogous rearrangement of electrons in the latter substance would formally lead also to formation of cyclohexanone and its anil, neither of which could be detected in the pyrolysate.



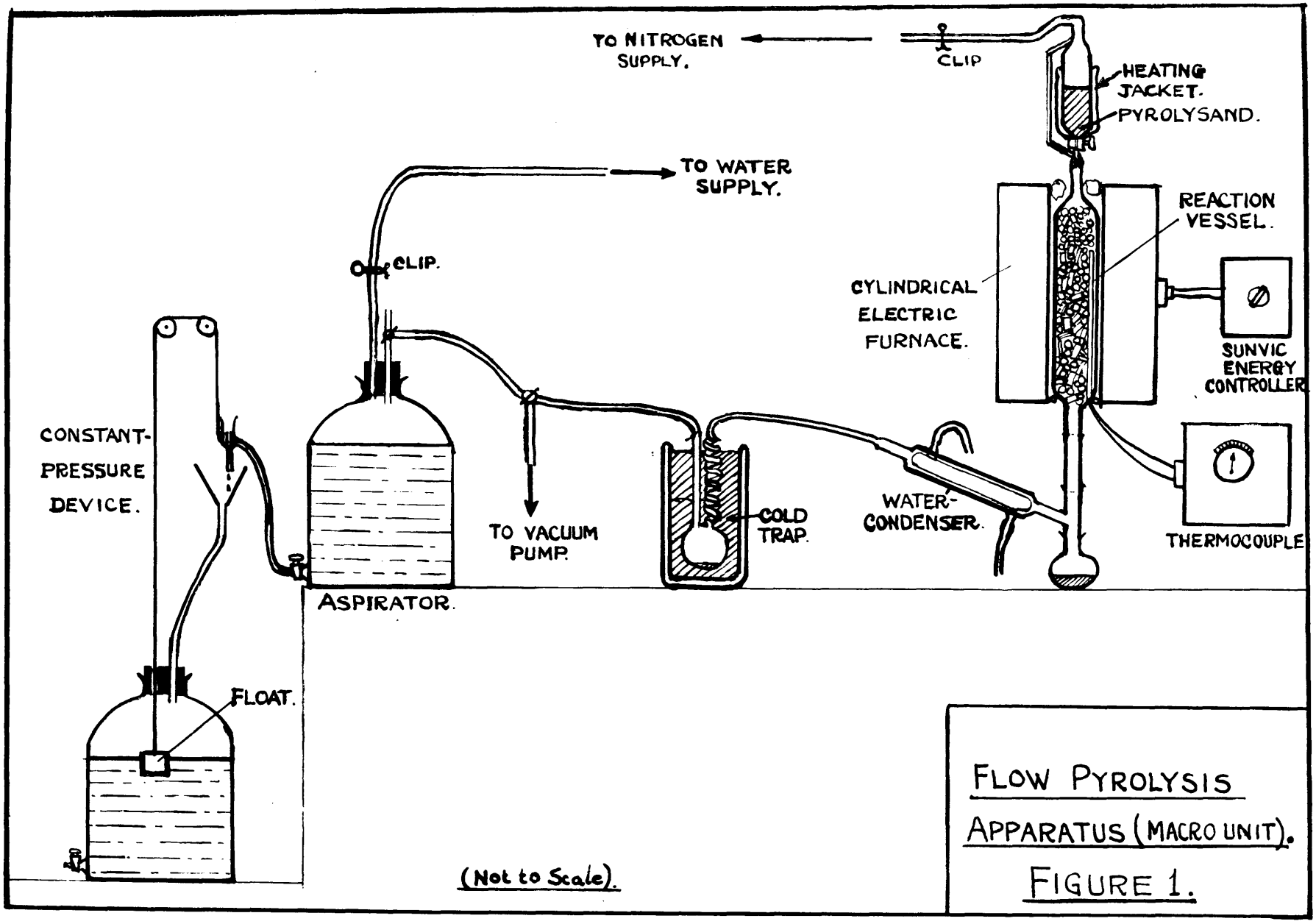
It is concluded, therefore, that replacement of an oxygen atom in the lactide ring by the >NPh group has the effect of stabilizing the ring to electronic rearrangement of the type envisaged for the pyrolysis of lactides.

A possible explanation may be that at the elevated temperature of pyrolysis (ca. 540°) the C-N bond of the -CO-NPh-group is strengthened by

migration of electrons as shown, aided by the electron-repelling inductive effect of the phenyl group and the electron-attracting inductive effect of the carbonyl oxygen atom:



If the spiro-lactone-lactam exists at 540° partly in the second canonical form shown, decomposition by the concerted mechanism proposed for lactides should be strongly disfavoured.



FLOW PYROLYSIS APPARATUS (MACRO UNIT).

FIGURE 1.

3. EXPERIMENTAL

3.1 Pyrolysis Apparatus and Procedure

3.1.1 Flow Pyrolysis : Macro Method

The flow pyrolysis apparatus used extensively for qualitative and semi-quantitative work is shown in Figure 1.

A Pyrex glass reaction vessel was used, of cylindrical central section, 12 in. long and 1.5 in. in diameter, packed with short lengths of Pyrex glass tubing. This vessel was supported vertically inside an electric furnace, of cylindrical construction, which kept the central section of the reaction vessel at a temperature of 500 ± 5°, regulated by a Sunvic energy controller. The temperature was measured by a chromel-alumel thermocouple, kept in a pocket located axially within the reaction vessel.

All pyrolyses were done in an inert atmosphere of nitrogen at atmospheric pressure. Before each run, the system was several times evacuated and thoroughly flushed with nitrogen to prevent combustion of the gases formed during pyrolyses. Cylinder nitrogen was freed from oxygen by passage through alkaline pyrogallol and concentrated sulphuric acid traps, the function of the latter trap being to remove water vapour.

Solid pyrolysands were introduced into the reaction vessel in the molten state by means of a tap-funnel, surrounded by an electric heating jacket which served to melt the pyrolysand. For pyrolysands that were liquid at room temperature, this pre-heating was, of course, unnecessary. The tap-funnel was fitted with a glass limb, connecting the spaces above and below the feed liquid, thereby equalising the pressures in this region.

Liquid and solid pyrolysis products emerging from the reactor were collected together in a first receiver after passage through a vertical air condenser. The gases leaving this point were then passed through an inclined water condenser to a second receiver, cooled in Drikold acetone. Volatile carbonyl compounds were removed from the gas stream by passage through a reagent trap containing 2:4-dinitrophenylhydrazine in 2N hydrochloric acid. The final, uncondensed gases were collected in a 20 l. aspirator, fitted with a self-adjusting constant-pressure device. The water in the aspirator was covered by a layer of liquid paraffin to prevent solution of water-soluble constituents of the gaseous pyrolysate.

During each run, pressure in the system was measured by manometers located above the dropping funnel and at the aspirator entry, so that a blockage in any part of the system could be detected. Another manometer measured the vacuum pressure during removal of oxygen from the apparatus.

The effective contact time for each run was calculated from the equation:[61]

$$t_c = \frac{43.9 \times V_c}{N_R \times T}$$

where t_c is the contact time in seconds,

V_c is the free, contact volume of the reactor, in ml.

N_R is the feed rate of the pyrolysand, in mole/hr.

and T is the absolute temperature.

Any carbonaceous or tarry deposits left in the reaction vessel were removed before each run by heating the vessel in the furnace at ca. 500° in a current of air.

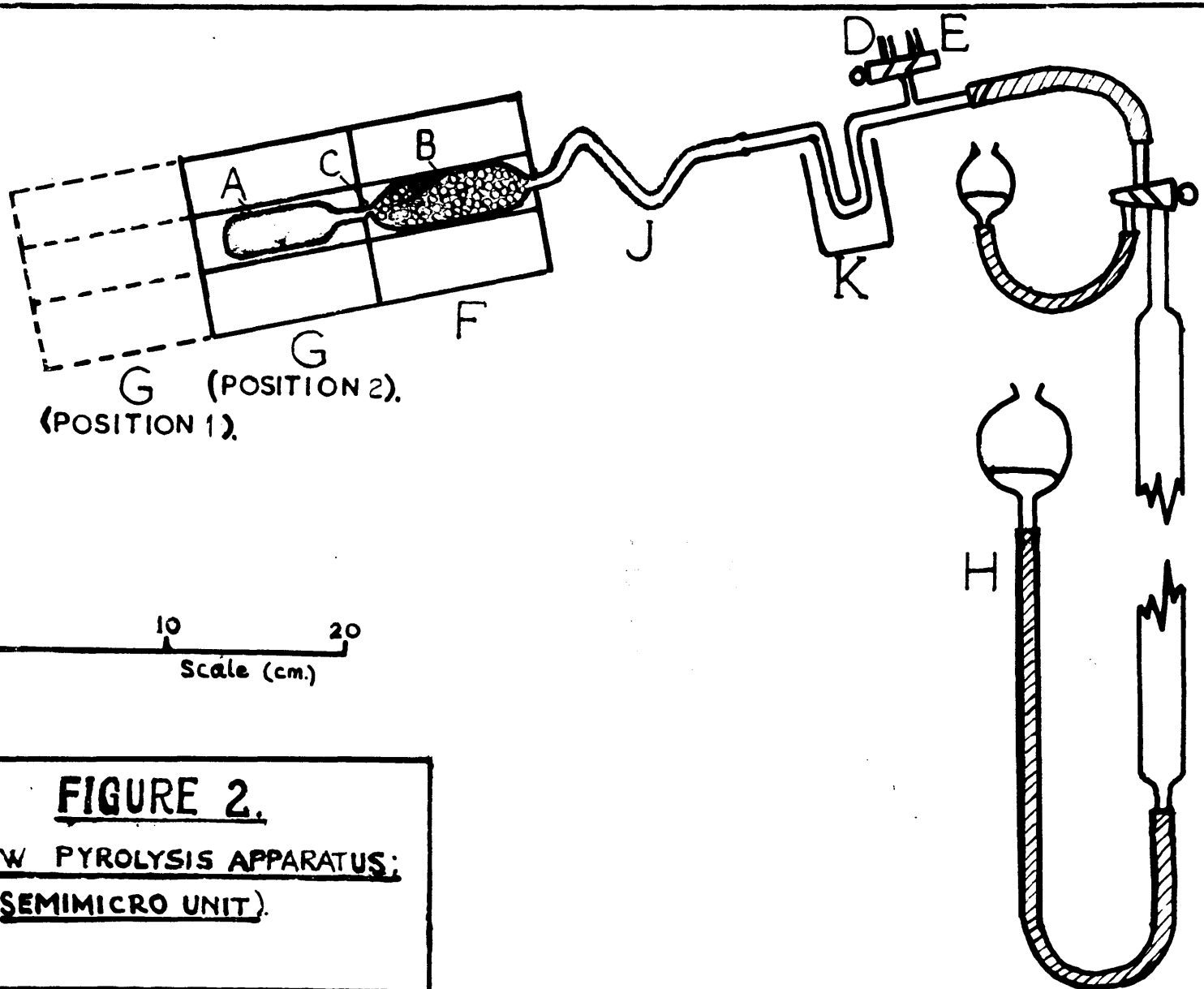


FIGURE 2.

FLOW PYROLYSIS APPARATUS;
(SEMIMICRO UNIT).

3.1.2 Flow Pyrolysis : Semimicro Method

The Pyrex glass apparatus shown in Figure 2 was used primarily for the collection and study of the gaseous pyrolysates from pyrolysands which were only available in small amounts. The pyrolysand (ca. 300 mg.) was placed in bulb A; bulb B was then filled with small Pyrex glass beads up to a constriction at C. The assembled apparatus was repeatedly evacuated and filled with nitrogen via inlets D and E. A short cylindrical electric furnace F, and the similar furnace G (in position 1), were maintained at 500° for a period of 2 hours, after which G was moved to position 2, enclosing bulb A. The gaseous pyrolysate was collected at approximately atmospheric pressure by adjustment of the barometric limb H during the run. Any non-gaseous pyrolysate was removed at the limb J or in the cold trap K.

After pyrolysis, which took about 10 min., the reactor was removed from the furnace and allowed to cool down to room temperature (about 15 min.). The total gas evolved was measured by the difference between the initial and final volume readings on the gas burette. By lowering the mercury level of the gas burette ca. 80% of the gaseous pyrolysate was collected for analysis, Sleigh's method[62] being a particularly suitable method of analysis.

3.1.3 Analytical Technique

Standard chemical methods of identification were employed throughout, solid products and derivatives being characterised by mixed melting point determinations (except for methylglyoxal bis-2,4 dinitrophenylhydrazone, for which paper chromatography was preferred). Gaseous

pyrolysates obtained by the macro-method were accurately analysed by a standard Hempel apparatus, supplemented by use of an alkaline potassium iodomercurate pipette for specific absorption of acetylene.[63] Gravimetric estimation of solid and liquid pyrolysates was, however, rendered approximate by the frequent complexity of the pyrolysates. In consequence, only an approximate estimation of the weight contribution of each competitive route to the overall breakdown scheme could be made for any given pyrolysand.

Standard identification methods were occasionally supplemented by the following special techniques:

Vapour-phase Chromatography

This highly sensitive technique was found particularly suitable for the detection and identification of liquid products of pyrolysis for which a sufficiently high degree of separation could not be obtained on fractional distillation of the pyrolysate. The instrument used in Part I of this thesis was the Griffin and George Mark IIB Vapour Phase Chromatograph, which is fitted with a katharometer detector. The length of the column employed was 6 feet, with a bore of 4 mm. The stationary phase was 30% w/w Silicone E.307 on celite (100 mesh), with nitrogen as carrier gas. The sample quantity used was 1 drop, introduced into the column by means of an Agla micrometer syringe. Comparison of the retention times of the various pyrolysis products in the column with those of a number of standards yielded rapid and accurate identification.

Infrared Spectrometry

Infrared spectrometry has been used to facilitate identification of

ethylene and propene in the vapour phase. The instrument used was the Perkin Elmer Infrared Spectrometer. Identification was achieved by comparison of the product spectrum with a number of standards.

Paper Chromatography

The paper chromatography technique described by Burton[64] was successfully applied to identify the nitrobenzene-soluble 2:4-dinitrophenylhydrazone derivative obtained from the pyrolysate from lactide(I) as methylglyoxal bis-2:4-dinitrophenylhydrazone. The stationary phase employed was a standard grade of paper (Whatman's No. 1), pretreated with a 70% aqueous solution of ethyl lactate. To pretreat the paper, it was immersed in the solution, drained, and allowed to become surface-dry in a current of air. Test spots of the unknown and standard derivatives were applied, and the chromatogram developed by the ascending technique in a tank presaturated with the solvent mixture - a 2% solution of carbon tetrachloride in petroleum ether (b.60-80°). The distances travelled by the spots were compared under ultra-violet light.

Colour test for anhydrides

A colour test, described by Davidson and Newman[65], has been used for the detection of linear anhydrides. The test depends on the production of a transient bluish-green coloration when an anhydride reacts with (p-nitrobenzamido)-phenylacetic acid in dry pyridine solution. The test is not applicable to cyclic anhydrides..

3.2 Preparation of Pyrolysands

3.2.1 Preparation of Lactide (I)

Lactide (I) was prepared by the slow distillation of commercial lactic

acid at 120 - 140° under reduced pressure, following the procedure of Carothers, Dorough, and van Natta[66]. On recrystallization from ethanol, (I) was obtained as colourless plates, m.p. 124° (Lit. 124.5°); yield 34%.

3.2.2 Preparation of the Lactide (II)

Acetone cyanohydrin was hydrolysed by concentrated hydrochloric acid to α-hydroxyisobutyric acid, following the method of Blaise[67]. The α-hydroxy acid was obtained as colourless needles from benzene, m.p. 79° (Lit. 79°), in 80% yield. The α-hydroxyisobutyric acid was subsequently converted to the lactide (II) by slow distillation at 190 - 220° according to the method of Blaise and Bagard[68]. Recrystallized from petroleum ether (b.40-60°), (II) was obtained as colourless prisms, m.p. 79° (Lit. 79°); yield 12% (Lit. 30%).

3.2.3 Preparation of the spiro-Dilactone (III)

cyclo-Hexanone was converted to its cyanohydrin by reaction with concentrated hydrochloric acid and sodium cyanide below 0°, following the procedure of Billiamoria and Maclagan[69]. Subsequent hydrolysis of the cyanohydrin with hot, concentrated hydrochloric acid[70] yielded 1-hydroxycyclohexanecarboxylic acid, obtained on recrystallization from petroleum ether (b.40-60°) as colourless plates, m.107 - 108° (Lit. 108°), in 55% yield, based on initial cyclohexanone.

The optimum conditions for the thermal conversion of 1-hydroxycyclohexanecarboxylic acid to (III) were first determined on a small scale by trial and error. The best yield was obtained by maintaining 20 g. of the hydroxy acid at ca.150° for 5 hours, during which time 0.5 cc. of

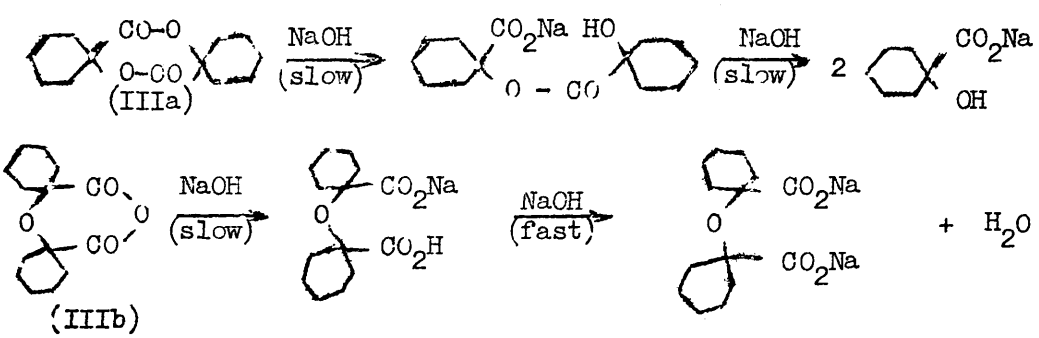
a mixture of water and cyclohexanone distilled out. Subsequent fractionation of the residue yielded a solid fraction, b. 125–160/6 mm., consisting mainly of undecomposed hydroxy acid, cyclohex-1-enecarboxylic acid, and (III). The acidic components were removed by treatment with saturated aqueous potassium bicarbonate solution, leaving a residue of (III), recrystallized from ethanol as colourless needles, m.p. 176°, yield 9.5% (for final stage). On scaling up the quantity of 1-hydroxycyclohexanecarboxylic acid used in the final stage, however, this yield fell to ca. 5%.

Found:	C, 67.0%;	H, 8.2%;	M (f.p. in benzene) 254
Calc. for $C_{14}H_{20}O_4$:	C, 66.7%;	H, 7.9%;	M 252

(III) has principal infrared absorption bands at wave numbers.

2867 (S), 1728 (S), 1454 (S), 1375 (M), 1266 (S),
1247 (S), 1159 (M), 1084 (S), 984 (S), 930 (M),
917 (W), 881 (M), 847 (W), 727 (W), cm^{-1}

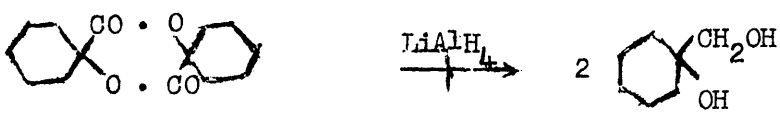
Whether (III) has the true lactide structure or that of its isomeric ether-anhydride (cf. analogous 1-hydroxycyclobutanecarboxylic acid derivatives[71]), cannot be determined by quantitative exhaustive hydrolysis, since for either structure, 2 equivalents of alkali would be used up per molecule.



(III)a would be expected to hydrolyse in two stages, kinetically, while (III)b should hydrolyse in a single stage, since the rate-determining step would be the opening of the anhydride ring.

Attempted hydrolysis to the first stage was unsuccessful, because of the extreme slowness of hydrolysis under mild conditions. Under the more forcing conditions found necessary to achieve hydrolysis, however, hydrolysis proceeded beyond the first and well into the second stage, so that no definite conclusion could be reached in this way.

It was thought that lithium aluminium hydride reduction of (IIIa) (cf. reduction of γ-valerolactone to pentandi-1:4-ol[72]) might result in formation of 1-methylolcyclohexan-1-ol (m.p.77°). Unfortunately reduction could not be achieved, possibly because of steric hindrance.



Since the pyrolytic behaviour of (III) (see below) is analogous to that of (I) and (II), it is considered to have the true lactide structure.

3.2.4 Preparation of Methylglyoxal

Following the procedure of Riley et al.,[73] methylglyoxal was prepared by the selenium dioxide oxidation of acetone. It was obtained as a yellow, mobile liquid, distilling under high vacuum at the ambient temperature (vapour condensed in liquid nitrogen). It very slowly polymerises on standing.

3.2.5 Preparation of isoPropyl α-Methylacrylate

The commercially obtained ester (ex Polymers Consultants Limited), purified by vacuum distillation, was a colourless liquid, b.p. 105°; 25-26/14 mm.

3.2.6 Preparation of α-Acetoxypropionic acid

Lactide acid was acetylated by a mixture of acetic acid and acetic anhydride, containing 4% of hydrogen chloride, by the method of Filachione and Fisher.[74] The α-acetoxypropionic acid thus obtained was a colourless liquid, b. 126 - 130°/11 mm. (Lit. 127°/11 mm.), in 65% yield.

Note: Solid α-acetoxypropionic acid has been variously reported in the early literature as colourless crystals, m. 39-40°[75], and m. 57 - 60°[76]. More recent preparations of the substance do not indicate the existence of a solid form, however, and the product obtained by the method described above did not deposit crystals on freezing, either in ice or in Drikold-acetone.

3.3 Results of Pyrolysis

The general conditions of pyrolysis are summarised in Table 1 (Runs 1 - 13 : macro-method) and Table 2 (Runs 14 and 15, semimicro-method); the temperature was 500° throughout. Detailed analyses are given below.

3.3.1 Pyrolysis of lactide (I) - Runs 1 and 2

Runs 1 and 2 gave concordant results; those of Run 1 are given here. Distillation of the main pyrolysate (b) yielded three fractions (i)-(iii) and a residue (iv) as follows:-

(i), b. 45-60°/15mm, (0.05 g.) was a white crystalline solid.

(ii), b. 60-80°/15mm, (0.7 g.) was a yellowish solid.

(iii), b. 70-150°/8mm, (11.5 g.) was an amber solid.

(iv), weighing 6.0 g., was a brown, tarry solid.

On testing each of these fractions in turn with aqueous sodium bicarbonate solution, no effervescence was observed; the main pyrolysate (b)

before fractionation, however, gave a slight positive reaction with the reagent, thus indicating the presence of a carboxylic acid.

Each fraction on recrystallisation from ethanol gave colourless crystals of (I), m.p. and mixed m.p. 124°.

Acrylic acid (b.p. 48.5°/15 mm.) could not be detected in fractions (i) or (ii) by vapour-phase chromatography.

A 2:4-dinitrophenylhydrazine reagent trap, placed between the main receiver and the cold trap, yielded a derivative, obtained as yellow needles, m.p. 158°, on recrystallisation from ethanol. A mixed m.p. determination with acetaldehyde 2:4-dinitrophenylhydrazone gave no depression.

A nitrobenzene-soluble portion of the crude product from the reagent trap was identified by paper chromatography as methylglyoxal bis-2:4-dinitrophenylhydrazone.

The gaseous pyrolysate (c) was shown by infrared analysis to contain ethylene. No but-1-ene or but-2-ene could be detected.

Other compounds sought, but with negative results, were the following:

pyruvic acid (b.p. 165° (decomp.); m.p. 14°);

acraldehyde (b.p. 52.5°);

ethyl acrylate (b.p. 101°);

2-methylbut-3-enoic acid (b.p. 95.5°/35 mm);

and α-acetoxypropionaldehyde (b.50 - 62°/33 mm).

3.3.2 Pyrolysis of the lactide (II) - Runs 3 and 4

The results of Runs 3 and 4 were in good agreement; those of Run 3 are given here.

Filtration of the main pyrolysate (b) yielded 3.5 g. of undecomposed starting material and a filtrate which on distillation yielded three fractions (i)-(iii) and a residue (iv):-

(i), b. 56 - 60°, (3.2 g.) was a clear liquid.

(ii), b. 60 - 80°, (4.2 g.) was a clear liquid.

(iii), b. 60 - 82°/25 mm (5.4 g.) was a pale yellow liquid.

(iv), weighing 7.5 g., was a brown tar, which, on cooling, deposited crystals of undecomposed (II), m.p. and mixed m.p. 79°.

Fraction (i) consisted mainly of acetone, characterised as its 2:4-dinitrophenylhydrazone, m.p. and mixed m.p. 127°.

Fraction (ii) was a mixture of acetone and α-methylacrylic acid (b.p. 161°), identified by vapour-phase chromatography. No 2:3-dimethylbut-2-ene (b.73°) could be detected.

Fraction (iii) was mainly α-methylacrylic acid, identified by vapour-phase chromatography; no isopropyl α-methylacrylate (b.p. 105°; 25-26°/14 mm.) could be detected.

A 2:4-dinitrophenylhydrazine trap yielded a product which contained the derivative of acetone only: α-methylacraldehyde 2:4 dinitrophenylhydrazone could not be detected by paper chromatography.

Infrared analysis of the gaseous pyrolysate (c) showed the presence of propene.

3.3.3 Pyrolysis of isopropyl α-methylacrylate - Runs 5 and 6

The results of Runs 5 and 6 were concordant; Run 5 is described here.

Attempted fractionation of the main pyrolysate (b) at atmospheric pressure yielded no distillate below 90°. Distillation under reduced pressure, yielded three fractions (i)-(iii) and a residue (iv).

(i), b. 25 - 40°/14 mm. (1.8 g.) was a clear liquid.

(ii), b. 40 - 57°/14 mm. (3.4 g.) was a pale yellow liquid.

(iii), b. 60 - 83°/14 mm. (3.1 g.) was a yellow liquid.

(iv), was a brown tar, weighing ca. 1 g.

Fraction (i) was shown by vapour phase chromatography to consist mainly of undecomposed isopropyl α-methylacrylate.

Fraction (ii) consisted of a mixture of isopropyl α-methylacrylate and α-methylacrylic acid (identified by vapour phase chromatography).

A 2:4-dinitrophenylhydrazine reagent trap yielded orange needles, m.p. 126°: a mixed m.p. with acetone 2:4-dinitrophenylhydrazone (m.p. 128°) gave no depression. No other 2:4-dinitrophenylhydrazones could be detected by paper chromatography.

Liquid (a) from the cold trap, raised to room temperature, evolved 0.24 l. of gas, identified by infrared spectrometry as propene.

3.3.4 Pyrolysis of the spiro-dilactone (III) - Runs 7 and 15

An exploratory semi-micro pyrolysis of (III) (Run 15) was followed by a more detailed study on the macro-scale (Run 7).

Filtration of the main pyrolysate (b) from Run 7 gave 15.7 g. of

white solid material and 7.8 g. of a yellowish liquid, which distilled at 140 - 168° leaving a small, tarry residue (ca.0.2 g.). No cyclohexylidenecyclohexane (b.p. 237° could be detected). The solid pyrolysate gave a faint effervescence with aqueous sodium bicarbonate solution, thus indicating the presence of a trace of a carboxylic acid.

The liquid pyrolysate yielded a 2:4-dinitrophenylhydrazone, m.p.160°; a mixed m.p. determination with the derivative of cyclohexanone (m.p.162°) gave no depression.

Vapour-phase chromatography of the total liquid pyrolysate detected only cyclohexanone; cyclohexene could not be detected.

3.3.5 Pyrolysis of lactide in the presence of free-radical inhibitor

Pyrolysis of lactide (I) containing 1% w/w of hydroquinone - Run 8

Fractionation of the main pyrolysate (b) yielded three fractions (i)-(iii) and a residue (iv) as follows:-

(i), b. 40-60°/15 mm. (0.5 g.) was a yellowish liquid.

(ii), b. 60-80°/15 mm. (0.6 g.) was a yellowish semi-solid.

(iii), b. 60-170°/8 mm. (10.2 g.) was an amber solid.

(iv), weighing ca.5 g., was a brown, tarry solid.

Fraction (i) contained acrylic acid, identified by vapour-phase chromatography.

Fraction (ii) consisted of a mixture of acrylic acid and undecomposed (I).

Fraction (iii) was mainly undecomposed (I).

A 2:4-dinitrophenylhydrazine trap yielded yellow prisms, m.p. 160°, identified as acetaldehyde 2:4-dinitrophenylhydrazone by a mixed m.p.

determination which gave no depression. Paper chromatography of a nitrobenzene-soluble portion of the crude product from the reagent trap detected the presence of methylglyoxal bis-2:4-dinitrophenylhydrazone.

Pyrolysis of the lactide (II) containing 1% w/w of hydroquinone-Run 9

The semi-solid pyrolysate (b) yielded on filtration 5.6 g. of undecomposed (II) and 21.4 g. of liquid. The latter on fractionation yielded two fractions, (i) and (ii), and a residue (iii).

(i), b. 56-69° (3.8 g.) was a pale yellow liquid.

(ii), b. 70-100°/14 mm. (4.8 g.) was an amber liquid.

(iii), weighing ca. 11 g., was a brown tar which, on standing, deposited crystals of undecomposed (II).

Fraction (i) was mainly acetone characterised as its 2:4-dinitrophenylhydrazone, m.p. 125°: mixed m.p. no depression.

Fraction (ii) contained mainly α-methylacrylic acid, identified by vapour-phase chromatography.

Pyrolysis of the spiro-dilactone (III) containing 1% w/w of hydroquinone - Run 10

The main pyrolysate (b) on filtration yielded 12.2 g. of white solid material and 2.5 g. of a liquid which distilled at 135-165°, leaving a small, tarry residue (ca. 0.2 g.)

The solid material gave a faint effervescence on testing with aqueous sodium bicarbonate solution, showing the presence of a trace of a carboxylic acid.

The liquid fraction yielded a 2:4-dinitrophenylhydrazone: yellow prisms m.p. 162°, identified as the derivative of cyclohexanone by a mixed m.p. determination, which gave no depression.

No cyclohexene could be detected by vapour phase chromatography.

3.3.6 Co-pyrolysis of lactide (I) and acrylic acid - Run 11

The pyrolysand consisted of a mixture of 25 g. lactide and 2.5 g. acrylic acid.

The main pyrolysate (b) on distillation yielded three fractions (i)-(iii) and a residue (iv), as follows:

Fraction (i), consisting of 0.5 g. of amber liquid, b. 40-60°/15 mm., contained mainly undecomposed acrylic acid (identified by vapour-phase chromatography).

Fraction (ii), an amber semi-solid (1.5 g.) b. 60-80/15 mm. contained acrylic acid (identified by vapour-phase chromatography) and undecomposed (I).

Fraction (iii) was an amber solid (6.9 g.) b.70-150°/8 mm., consisting mainly of undecomposed (I).

The residue (6.0 g.) was a dark brown tar.

Acetaldehyde was identified as its 2:4-dinitrophenylhydrazone, m.p. and mixed m.p. 160°, obtained from a reagent trap placed in the pyrolysis system.

3.3.7 Pyrolysis of α-acetoxypropionic acid - Runs 12 and 13

Runs 12 and 13 gave concordant results: those for Run 12 are given here.

The main pyrolysate (b) before fractionation gave a positive colour test with the Davidson-Newman reagent[65] and with anhydrous copper sulphate, indicating the presence of an anhydride and water respectively. On fractionation, (b) yielded three fractions (i)-(iii) and a small, tarry residue:-

Fraction (i), a yellow liquid (5.0 g.) b. 16-100°, consisted mainly of acetaldehyde (identified as its 2:4-dinitrophenylhydrazone: m.p. and mixed m.p. 162°) and acetic acid (identified by vapour phase chromatography).

Fraction (ii), a yellow liquid (8.3 g.) b. 100-130°, consisted mainly of acetic acid and acetic anhydride (both identified by vapour-phase chromatography).

Fraction (iii), a yellow liquid (2.1 g.) b. 90-100°/15 mm., was similar to fraction (ii) in composition, containing mainly acetic acid and acetic anhydride.

A 2:4-dinitrophenylhydrazine reagent trap placed in the pyrolysis system yielded a crystalline derivative, identified as that of acetaldehyde: m.p. and mixed m.p. 160°. The product from this trap was completely soluble in ethanol - a fact which excludes the likelihood of formation of methylglyoxal as an intermediate during pyrolysis.

No acrylic acid could be detected by vapour-phase chromatography of the various fractions.

3.3.8 Semi-micro pyrolysis of methylglyoxal - Run 14

The liquid (a) in the air-cooled limb of the apparatus gave a 2:4-dinitrophenylhydrazone identified by paper chromatography as that of methylglyoxal.

Liquid (b) yielded a mixture of 2:4-dinitrophenylhydrazones. Repeated extraction of the crude product with ethanol yielded yellow needles, m.p. 159°, identified as acetaldehyde 2:4-dinitrophenylhydrazone by the method of mixed m.p., which gave no depression. The remainder, soluble in nitrobenzene, was identified by paper chromatography as methylglyoxal bis-2:4-dinitrophenylhydrazone.

Note: The gaseous pyrolysate (c) almost certainly contained a large proportion of acetaldehyde, because of the inefficiency of the Drikold trap in cooling the relatively hot, rapid stream of acetaldehyde vapour emerging from the furnace.

Thus the uncondensed acetaldehyde and any carbon dioxide formed are reported together, both being soluble in the aqueous sodium hydroxide used in the gas analysis apparatus.

TABLE 1

Flow Pyrolyses Using the Macro-Pyrolysis Apparatus

Run No.	1	2	3	4
Reactor Temperature (°C)	500°	500°	500°	500°
Pyrolysand	(I)	(I)	(II)	(II)
Feed Rate (g./min.)	0.32	0.29	0.41	0.39
Contact Time (sec.)	134	148	125	131
Wt. Pyrolysed (g.)	35	35	35	30
(a) in Cold Trap (ml.)	nil	nil	nil	nil
(b) in Main Receiver (g.)	21.0	16.0	25.1	21.4
(c) Gaseous Pyrolysate (l)	7.8 { CO_2 9.0%, Uns. 2.0%, CO 89.0% }	10.9 { CO_2 7.3%, Uns. 0.9%, CO 91.8% }	3.6 { CO_2 6.8%, Uns. 1.9%, CO 91.3% }	3.8 { CO_2 11.3%, Uns. 3.2%, CO 85.5% }

TABLE 1 (Continued)

Run No.	5	6	7	8
Reactor Temperature (°C)	500°	500°	500°	500°
Pyrolysand	iso-Propyl Methacrylate	iso-Propyl Methacrylate	(III)	(I) + Hydroquinone (1%)
Feed Rate (g./min.)	0.38	0.45	0.23	0.29
Contact Time (sec.)	100	85	328	148
Wt. Pyrolysed (g.)	35	30	28	35
(a) in Cold Trap (ml.)	2	1.5	nil	nil
(b) in Main Receiver (g.)	28.1	23.5	23.5	17.5
(c) Gaseous Pyrolysate (l)	1.4 { CO_2 16.9%; Uns. 49.1%; CO 34.0% }	1.2 { CO_2 17.6%; Uns. 30.3%; CO 52.1% }	1.8 { CO_2 9.8%; Uns. –; CO 90.2% }	8.8 { CO_2 8.6%; Uns. 5.2%; CO 86.2% }

TABLE 1 (Cont'd.)

Run No.	9	10	11	12	13
Reactor Temperature	500°	500°	500°	500°	500°
Pyrolysand	(II) + hydroquinone (1%)	(III) + hydroquinone (1%)	(I) + acrylic acid	α-acetoxy-propionic acid	α-acetoxy-propionic acid
Feed Rate (g./min.)	0.44	0.17	0.34	0.39	0.35
Contact Time (sec.)	117	447	142	101	112
Wt. Pyrolysed (g.)	35	17	27.5	35	35
(a) in Cold Trap (ml.)	nil	nil	nil	nil	nil
(b) in Main Receiver (g.)	27	14.7	16.0	18.1	19.0
(c) Gaseous Pyrolysate (l.)	2.6 { CO_2 / Uns. / CO	0.4 { CO_2 / Uns. / CO	4.9 { 17.6 / 2.1 / 80.3	8.5 { 2.1 / – / 97.9	8.7 { 2.3 / – / 97.7

TABLE 2

Flow Pyrolyses Using the Semi-micro Pyrolysis Apparatus

Run No.	14	15
Reactor Temperature (^{o}C)	500^{o}	500^{o}
Pyrolysand	Methylglyoxal	(III)
Weight Pyrolysed (g.)	0.411	0.374
(a) in Air-cooled limb (ml.)	0.2	0.2
(b) in 'Drikold' limb (ml.)	0.1	nil
(c) Gaseous Pyrolysate (ml.)	88.0 { CO 70.3%; MeCHO + CO_2 29.7% }	55 { CO 97.7%; CO_2 2.3% }

PART II

PYROLYSIS OF POLY(DIETHYL MALEATE-METHYL α-METHYL ACRYLATE)

1. INTRODUCTION

1.1 Polyester Resins, their Manufacture and Uses

Unsaturated polyester resins have recently become established commercially, in the form of laminates, for such diverse purposes as the manufacture of car bodies, the hulls of ships up to the size of medium launches, and aeroplane radome housings.

Resins of this type are made by copolymerising an unsaturated polyester, usually poly(ethylene fumarate), with an unsaturated monomer of the vinyl type, e.g. styrene or methyl α-methylacrylate, on a supporting structure of glass fibre, cloth, paper, or the like. The laminates thus formed are strong, light, and highly corrosion-resistant. They also have excellent thermal and electrical characteristics.

Their greatest advantage, however, is undoubtedly their ease of fabrication, since high pressures and elaborate moulding equipment are not required. The resins liberate no volatile products on setting, and can thus be moulded at very low pressures - hence the term "contact resins." Commercially, unsaturated polyester resins are usually supplied as a syrup containing three essential components - unsaturated polyester, vinyl monomer, and inhibitor. The presence of an inhibitor is necessary to prolong the storage life of the product before it is cured. *tert.*-Butyl catechol, hydroquinone, and quinone are among the most effective inhibitors used.

Copolymerisation is generally initiated by dissolving a peroxide-type catalyst (usually benzoyl peroxide) in the resin and heating for a short time. Laminates are prepared by spreading successive layers of the filling material and resin on a mould of the desired shape, and curing.

Resins are available that will cure in a few hours at room temperature, while others cure in as little as $\frac{1}{2}$ minute at 110°.[77]

For economic reasons, styrene is the vinyl-type monomer most often employed. Ethylene glycol and maleic anhydride, both cheap and readily available, are the most common difunctional alcoholic and acidic components used in the preparation of the polyester.

The mechanical properties of unsaturated polyester resins can be varied from strong, rigid materials to tough, flexible ones by a suitable choice of the following variables:

(i) the type of dihydric alcohol used;

(ii) the type of dibasic acid used;

(iii) the ratio of saturated to unsaturated dibasic acid [to increase the flexibility of the product, the double bonds of the unsaturated polyester can be spaced out by adding a long-chain saturated dibasic acid during polycondensation];

and (iv) the type and amount of vinyl monomer used.

Special characteristics can be imposed upon the resins by different combinations of these variables. The resin of particular interest in the present work, for example, poly(ethylene fumarate-methyl α-methylacrylate) (IV), has been used to make vitreous, transparent plastics which are stable to light.[78]

The thermal degradation of (IV) has been found to yield products of such complexity[55] that accurate analysis is practically impossible. Part II of this thesis describes an investigation of the mode of thermal break-

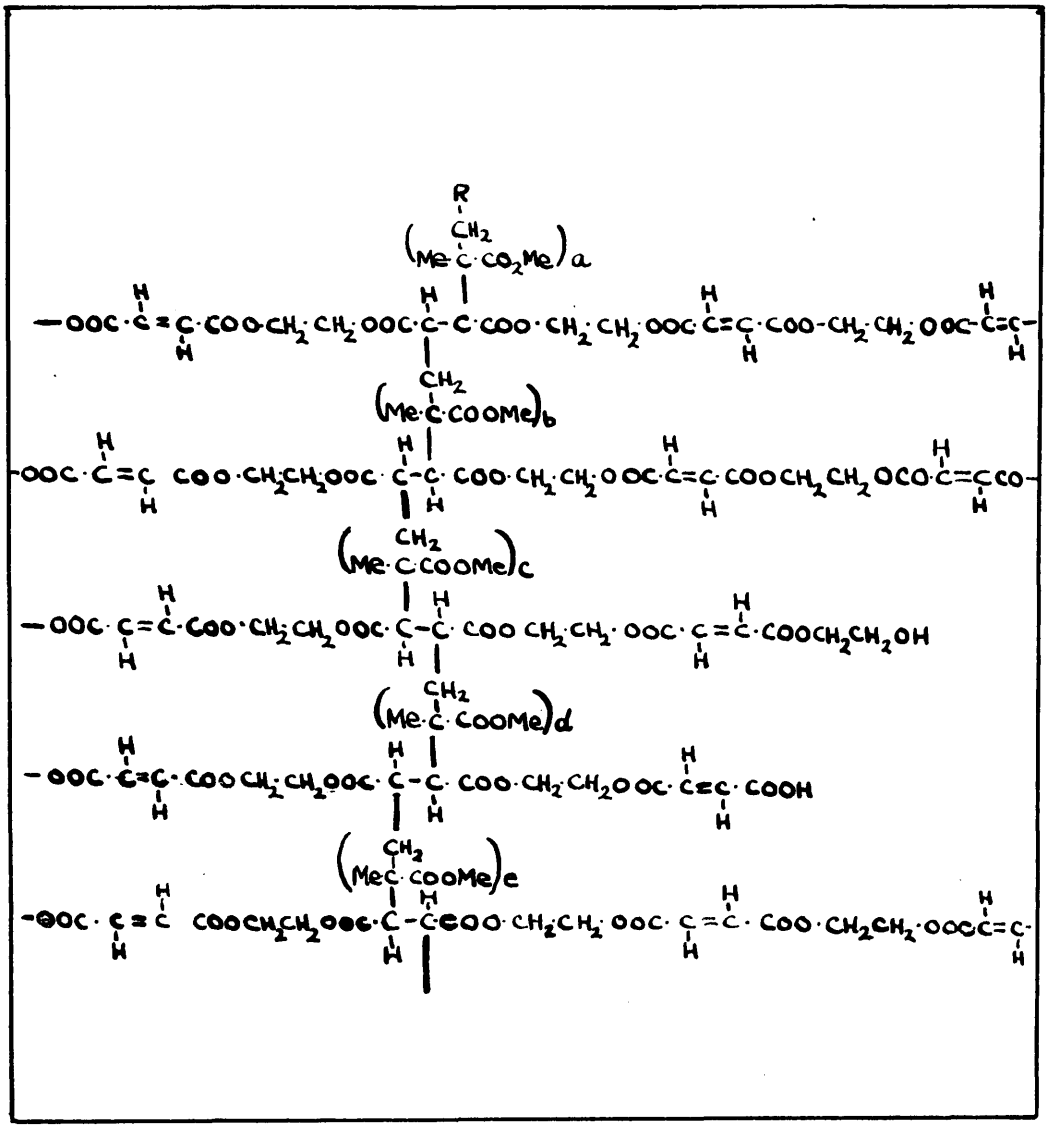


FIGURE 3.

REPRESENTATION OF MACROMOLECULAR STRUCTURE OF POLY(ETHYLENE FUMARATE-METHYL α-METHYLACRYLATE).

R : Catalyst residue.

a, b, c, d, etc. ca. 18 for equimolar α-methylacrylate and fumarate feed ratio.

down of the cross-linking polyvinyl chains in (IV), using the relatively simple copolymer poly(diethyl maleate-methyl α-methylacrylate) (V) as a model.

1.2 Chemical Constitution of Polyester Resins

When an unsaturated polyester resin sets, the unsaturated polyester chains are rapidly cross-linked by copolymerising with the vinyl monomer, yielding ultimately a rigid, three-dimensional macromolecular network. (IV), for example, would have the partial structure represented in Fig.3.

Successful fabrication of reinforced laminates from these resins requires a knowledge of the relationship between the ratio of starting components and the composition of the resin produced.

A general equation has been formulated for the ideal copolymerisation of two simple unsaturated monomers, A and B, as follows:

$$\frac{dA}{dB} = \frac{A}{B} \quad \frac{(r_1 + \frac{B}{A})}{(r_2 \frac{B}{A} + 1)}$$

where $\frac{dA}{dB}$ is the instantaneous relative rate of entry of the monomers into the copolymer,

A and B are the instantaneous concentrations of A and B respectively, and r_1 and r_2 are the reactivity ratios for A and B respectively, under the experimental conditions employed.

The reactivity ratios for a given pair of monomers are parameters which give a direct measure of the relative tendencies of the growing radical of each species, A or B, to combine with a monomer molecule of its own kind rather than with a molecule of the comonomer during chain

propagation. For a given set of conditions, therefore, the reciprocal reactivity ratio of each monomer in the system is a direct measure of the alternating tendency of its own radical.

The above equation can generally be applied to the initial stages of copolymerisation of A and B when A and B are the initial concentrations of the two monomers respectively, provided, of course, that neither monomer is being used up too quickly relative to the other.

To evaluate the reactivity ratios of a given monomer pair, it is necessary to determine the composition of the copolymers obtained from a series of monomer mixtures of known composition. Copolymer analysis is much more readily achieved, however, for a simple copolymer system, e.g. poly(styrene-methyl α-methylacrylate) than for a cross-linked unsaturated polyester resin. Experimental difficulties, especially the high insolubility of the resins, have so far deterred attempts to measure the reactivity ratios of the two types of unsaturation initially present. Such difficulties have been successfully overcome in these laboratories by Gordon et al.[79] for the resin (IV) by a special "swelling and extraction" technique of purification and analysis of the resin formed in the initial stages of copolymerisation. An average bridge-length of 18 methyl α-methylacrylate units was hence calculated for the resin formed from an equimolar feed mixture of each type of unsaturation.

Frisch and Stannett[80] were the first to use model systems to determine the mean bridge-length between adjacent chains, thus reducing the analytical difficulties inherent in unsaturated polyester resins. They selected

diethyl maleate as a suitable model for the unsaturated polyester, poly (ethylene maleate), prepared by polycondensation of maleic anhydride with ethylene glycol. With a knowledge of the reactivity ratios of the monomer pair styrene and diethyl maleate, they deduced an average bridge-length of 8 styrene units for poly (ethylene maleate-styrene), prepared from an equimolar feed ratio of each type of unsaturation.

Although the choice of diethyl maleate as a model appeared to be appropriate at first sight, more recent work[79] has shown that in the above polycondensation, conversion of maleic to fumaric unsaturation is substantially complete.

This discovery led Wycherley[81] to select diethyl fumarate rather than diethyl maleate as a suitable model for the unsaturated polyester. From the known reactivity ratios of diethyl fumarate and styrene, he calculated the average number of styrene units per cross-link to be 1.2, starting with an equimolar feed.

A similar estimate of the number of cross-linking monomer units per bridge was obtained by Hayes and Hunter[82] for poly(propylene fumarate - styrene). Complete hydrolysis of the copolymer obtained from an equimolar feed gave a fumaric acid-styrene copolymer, from the analysis of which the average number of styrene units per bridge was estimated to be ca. 1.6

Application of the above relatively simple copolymerisation equation to the cross-linking of an unsaturated polyester is subject to several qualifications:

(i) There must be no excessively rapid depletion of the cross-linking monomer, as explained above.

(ii) It must be assumed that the reactivity of fumaric double bonds is independent of the nature of the attached ester groups - here pendant polyester chains.

(iii) The copolymerisation equation is only applicable to low conversions, such as occur up to the gel point, since, after formation of the cross-linked macromolecule, the reaction conditions change. The diffusibility of unreacted double bonds in the polyester chains may well be reduced, with corresponding decrease in their reactivity. Those double bonds which are located near a point of cross-linking may also be blocked by steric hindrance.

(iv) Effects such as chain transfer are not taken into account by the equation. Robertson and Shepherd[83] applied the equation to calculate the composition of several polyfumarate resins, and correlated the mechanical strength with the degree of cross-linking. The vinyl acetate- and styrene- polyfumarate resins were found to be mechanically stronger than the corresponding methyl α-methylacrylate and acrylonitrile resins. The higher degree of cross-linking calculated for the former pair (using model systems) was thought to be responsible for this. The relationship broke down, however, when applied to the corresponding methyl acrylate resin, which was surprisingly strong, although it had a low calculated degree of cross-linking. This has been attributed to a high true degree of cross-linking of the resin, associated with chain transfer, since the bulk

polymerisation of methyl acrylate is known to be prone to chain transfer and consequent gelation.[84] Although the bulk polymerisation of vinyl acetate may under certain conditions proceed with cross-linking,[85] the vinyl acetate resin is so tightly cross-linked that the effects of transfer are not obvious.

1.3 Pyrolysis of Poly(ethylene fumarate - methyl α-methylacrylate and Related Polymeric Systems

The resin which has hitherto received most attention in these laboratories is (IV), for which Gordon et al[79] evaluated the monomer reactivity ratios. Two main reasons suggest this resin as a model for study, in preference to poly (ethylene fumarate-styrene):

(i) Poly (ethylene fumarate) is soluble in methyl α-methylacrylate, whereas in styrene it is not, and the latter copolymerisation system is complicated by the necessary addition of a third monomer or solvent.

and

(ii) The degradation characteristics of poly(methyl α-methylacrylate) are somewhat less complex than those of polystyrene (see below).

Exploratory pyrolyses of (IV) by Mackinnon[55] have shown that degradation of the polyvinyl chains commences at a lower temperature than that of the polyfumarate chains. Depolymerisation appeared to start at the ends of the poly(methyl α-methylacrylate) chains and to be terminated at the first point of cross-linking with a fumarate unit, as indicated by the evolution of a markedly lower yield of monomeric methyl α-methylacrylate from the degrading resin than from the simple homopolymer, poly(methyl α-methylacrylate), pyrolysed under the same conditions

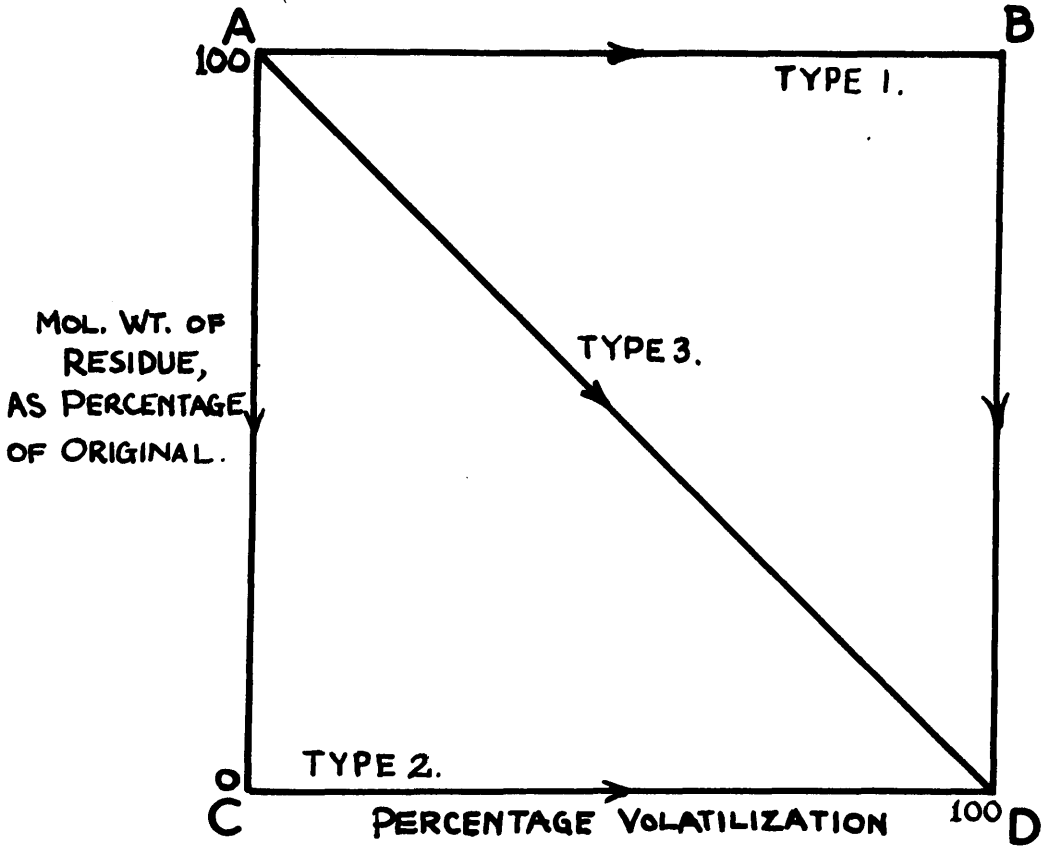


FIGURE 4.

Theoretical Modes of Thermal Breakdown of High Polymers.

(based on the actual methyl α-methylacrylate content of each system).

Accurate qualitative and quantitative analysis of the degradation products of the cross-linked polyester resin were, however, precluded by the structural rigidity of the macromolecule, which hinders the escape of volatile products and thus enables complicating secondary reactions to occur. Perhaps the most important conclusion emerging from Mackinnon's work is that, as the working temperature of the resin is raised, degradation of the poly(methyl α-methylacrylate) chains will probably be the primary source of failure. The need for a further study of the degradation characteristics of the polyvinyl chains in (IV), e.g. by pyrolysis of relatively simple models, is thus apparent.

1.3.1 Pyrolysis of Vinyl Polymers

Theoretically, the degradation of polymers derived from vinyl-type monomers may follow one of three courses,[86] as shown in Fig. 4.

Type 1, represented by the line ABD, is characteristic of chain depolymerisation, a free radical process which is essentially the reverse of polymerisation. Entire molecules of the polymer are rapidly converted to monomer, which escapes from the system as a vapour, the molecular weight of the residual polymer remaining constant throughout degradation.

Type 2, represented by ACD, is characteristic of random degradation, i.e. scission of the polymer at random points along the chain, resulting in a rapid drop in molecular weight.

Type 3, represented by the diagonal AD, is intermediate in character. Pyrolysis proceeds by the successive breaking-off of short fragments, up

to a few monomer units in length, from the degrading chain-end, resulting in stepwise reduction of the molecular weight of the polymeric residue.

The exclusive pyrolysis of a polymer by any one of these basic processes is not usually encountered in practice; the predominating type of degradation undergone by a particular polymer is dictated by the experimental conditions, especially the temperature.

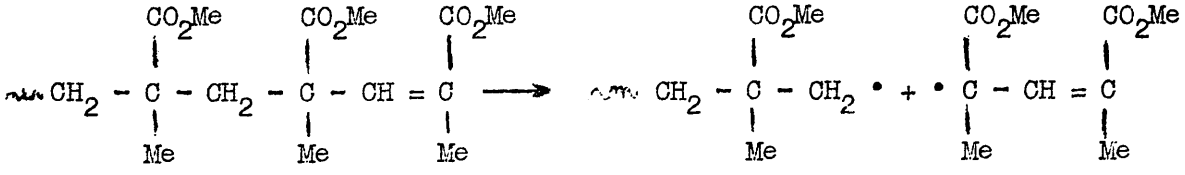
1.3.2 Pyrolysis of Polystyrene

The thermal degradation of polystyrene has been investigated by Jellinek[87] and by Madorsky[88], according to whom two distinct mechanisns are involved, one operating below and the other above ca. 340°. Below 340°, only slight volatilization (a few per cent) occurs, but there is a rapid decrease in molecular weight. The fall in molecular weight has been attributed to breakage of weak links in the polystyrene chains, possibly formed either by hydroperoxidation of a limited number of tertiary hydrogen atoms by molecular oxygen during storage, or by the copolymerisation of molecular oxygen (present as an impurity) into the polystyrene during polymerisation. At higher temperatures, further decomposition occurs, by a different mechanism. After the weak link scission phase of the reaction, there ensues a steady evolution of monomer, dimer, trimer, tetramer etc., while the molecular weight of the non-volatile residue decreases almost linearly to zero at 100% conversion. This latter behaviour approximates to degradation Type 3 (see above).

1.3.3 Pyrolysis of Poly(methyl α-methylacrylate)

The thermal degradation of poly(methyl α-methylacrylate) also occurs by a low- and a high-temperature mechanism, with a critical temperature of

ca. 300° [89]. For a polymer of initial number average molecular weight (M_n) of up to 500,000, depolymerisation at 220° has been shown by Grassie and Melville[86] to be initiated at the chain-ends, and to proceed by a kind of "unzippering" action in which successive monomer units are rapidly removed from the degrading chain-end - essentially degradation of the above Type 1. The molecular weight of the polymeric residue remains approximately constant over a large part of the degradation process, but falls slightly in the later stages. (This fall in molecular weight occurs sooner for higher molecular weight polymers ($M_n > 500,000$), for which the kinetic chain length of depolymerisation is less than the degree of polymerisation. For such polymers, incomplete decomposition of degrading molecules leaves fragments of shorter chain length, which lower the average residual molecular weight). At 220°, only ca. 50% of the polymer is degradable; the remaining half is much more stable, and must be heated to ca. 300° before it too undergoes breakdown. In the polymerisation of methyl α-methacrylate at 60° [90], chain termination occurs entirely by disproportionation, and therefore half of the polymer molecules in a given sample must contain a double bond at one end. It has been proposed[91] that those chains containing a terminal double bond undergo primary activation by the removal of an allyl-type radical from the chain-end.



This process requires the input of much less energy than the rupture of an

ordinary C - C bond, since conjugation energy, which may reach 23 kcal. per mole, is liberated in the removal of the relatively stable allyl-type radical. To prove that a double bond is needed for chain-end initiation, Grassie and Melville[86] used different methods of polymerisation (e.g. polymerisation with chain transfer agents) whereby it was possible to regulate the proportion of molecules which have terminal double bonds. It was found that only the polymer molecules containing such double bonds can be degraded at 220°. Brockhaus and Jenckel[92] finally confirmed this by quantitative permanganate determination of the number of terminal double bonds in the polymer, done in parallel with measurements of the degradation rate.

At higher temperatures (above 300°), Hart[93] has shown degradation to proceed with a sharp initial fall in molecular weight, which then diminishes gradually towards zero at 100% depolymerisation. The reason underlying this behaviour has been shown to be random rupture of the C - C bonds in the polymer chain backbone (cf. Type 2, above); this leads to formation of new radical ends, at which chain depolymerisation can recommence.

The monomer yield, and monomer content of the products of degradation obtainable from polystyrene and poly(methyl α-methylacrylate) are very different. Whereas ca. 90% of methyl α-methylacrylate is recoverable from poly(methyl α-methylacrylate), only ca. 40% of monomeric styrene is obtained from polystyrene. The volatile product from poly(methyl α-methylacrylate) is ca. 100% monomer, but for polystyrene, there is only ca. 42% of styrene in the volatile product. (All percentages are on a weight basis).

It is apparent from the foregoing summary that any deviation from normal pyrolytic behaviour produced by the incorporation of isolated comonomer units into the polymer would be more readily detected for the poly(methyl α-methylacrylate) than for the polystyrene system, at temperatures below 300°.

1.3.4 Pyrolysis of Copolymers

Although much work has been done on the pyrolysis of linear addition homopolymers, relatively little has been done on copolymers.

Wall[94] pyrolysed at ca.425° a number of copolymers and related the variation in the yield of the individual monomers to the composition of the copolymers studied. The chief quantity studied by Wall was the "relative monomer yield", which is the yield of a monomer obtained from the copolymer divided by the yield of the same monomer from its simple homopolymer, pyrolysed under the same conditions. According to Wall, there are two distinct ways in which the individual monomer yields may be decreased. For a copolymer derived from two monomers, A and B, these are:

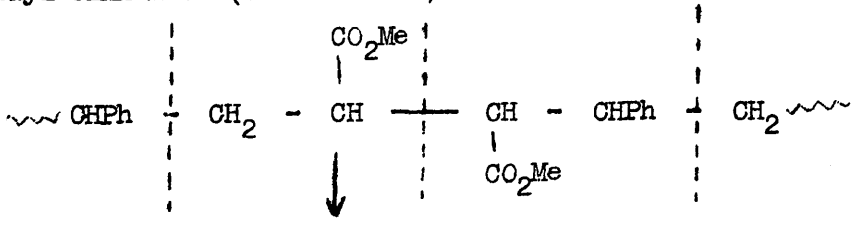
(i) Preferential formation of co-dimer (or co-trimer) at the boundaries between sequences of A and B units;

or (ii) Formation of hybrid monomers, which may be formed from fragments of adjacent A and B units by rupture of the internal bonds of these units.

Examples of copolymers studied thus by Wall include poly(styrene-methyl α-methylacrylate), poly(dimethyl fumarate-styrene), and poly(stilbene-methyl α-methylacrylate).

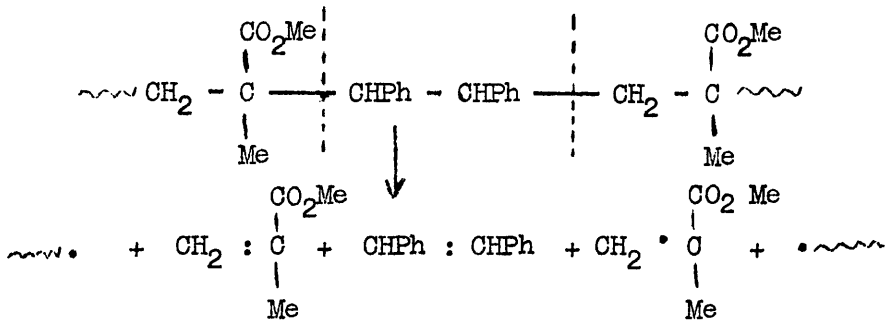
As described above, poly(methyl α-methylacrylate) and polystyrene differ in their pyrolytic behaviour in that monomeric methyl α-methylacrylate is the sole volatile product from the former, whereas styrene, its dimer, trimer etc. are formed from the latter. The relative yield of styrene obtained from poly(styrene-methyl α-methylacrylate) was found to have been increased, whereas the relative yield of methyl α-methylacrylate was unchanged. The enhanced relative yield of styrene illustrates the lower tendency of methyl α-methylacrylate to form dimers compared to styrene. A certain number of styrene units in the copolymer, being isolated between the other monomer units, are thus restrained from dimerising with their own kind. The unaffected relative yield of methyl α-methylacrylate, on the other hand, is as expected, since dimer formation is not favoured, and it is structurally obvious that no hybrid monomer effect can deplete the yield.

Poly(dimethyl fumarate-styrene) on pyrolysis yielded, in addition to the original monomers, a minor amount of methyl acrylate. This was taken to indicate some preferential splitting of the internal C-C bonds of the original monomer units, with formation of the hybrid monomers, methyl acrylate and methyl cinnamate (not detected) as shown:



$$\sim\!\!\sim CHPh\cdot + CH_2{:}CH\cdot CO_2Me + Ph\cdot CH{:}CH\cdot CO_2Me + \cdot CH_2\sim\!\!\sim$$

Poly(stilbene-methyl α-methylacrylate), on the other hand, yielded on pyrolysis only the original monomers. It was concluded that this copolymer undergoes thermal degradation by the breaking of the bonds originally formed during copolymerisation:



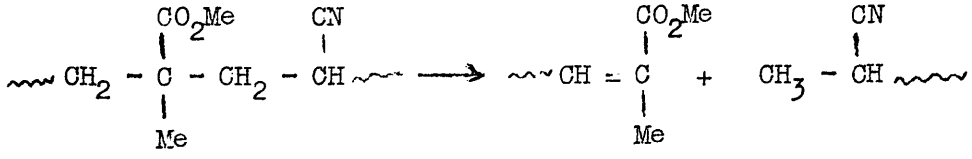
Further interesting examples of hybrid monomer formation have been brought to light in a recent paper by Haszeldine et al[95]. A new type of copolymer has been produced by copolymerising perfluoroalkyl nitroso-compounds, R_FNO, with olefins. The N=O group acts like a C=C group, so that the repeat unit in the 1:1 copolymer usually obtained is -N-O-C-C-. Thus, for example, trifluoronitrosomethane reacts with tetrafluorethylene below room temperature to give a 1:1 copolymer:

$$CF_3NO + CF_2 : CF_2 \longrightarrow \left[-N-O-CF_2-CF_2-\right]_n$$

Pyrolysis of this copolymer at ca. 550° in vacuo. yields as the exclusive volatile products equimolar amounts of the hybrid monomers carbonyl fluoride, COF_2, and perfluoro(methylenemethylamine), $CF_3 \cdot N = CF_2$. The hybrid monomer effect has been reported only for pyrolysis at elevated temperatures, well above 300°, at which temperature random rupture of the C-C bonds in the chain backbone occurs.

In addition to these studies of the nature of the volatile products obtained on pyrolysis of copolymers, there is one recorded account of the accompanying changes that occur in the molecular weight of the residual copolymer. This is the study by Grassie and Melville[86,96] of the thermal degradation of poly(acrylonitrile-methyl α-methylacrylate). The degradation characteristics of poly(methyl α-methylacrylate) were found to be fundamentally altered by incorporation in the chains of minute amounts of acrylonitrile. Kinetic measurements on the degrading copolymer at 220° showed that, instead of starting at maximum rate, as for poly(methyl α-methylacrylate), there was an induction period, accompanied by a rapid fall in number-average molecular weight. Later in the reaction, Mn levelled off to a value corresponding to chain scission in the region of every acrylonitrile unit spaced out along the chains. The introduction of occasional acrylonitrile units into the poly(methyl α-methylacrylate) chain was thus found to lead to formation of points of thermal instability.

The most plausible mechanism suggested by Grassie and Melville to explain these phenomena, particularly the induction period, was disproportionation into two stable molecules at the junction of an acrylonitrile unit with a methyl α-methylacrylate unit:



The increasing concentration of the former end-structure, identical

with the unsaturated chain-ends of poly(methyl α-methylacrylate), was thought to account for the induction period. Several anomalous results were obtained, however, so that the above mechanism could not definitely be established.

Objects of Research

The primary object of Part II of this work is to elucidate, by means of a relatively simple model system, the pyrolytic breakdown mechanism(s) of the cross-linking poly(methyl α-methyacrylate) chains in (IV), and hence, if possible, suggest improvements whereby the thermal stability of the resin might be improved.

Poly(diethyl maleate-methyl α-methylacrylate) (V), for which the monomer reactivity ratios are known[97], has been chosen as a suitable model for a systematic, quantitative pyrolytic study of this kind.

In view of the observation by Grassie and Melville[86,96] that thermal chain scission occurs in the region of each isolated acrylonitrile unit in poly(acrylonitrile-methyl α-methylacrylate), pyrolysed at 220°, the idea occurred to the present author that for copolymers of methyl α-methylacrylate containing only occasional isolated comonomer units, studies of the molecular weight changes during pyrolysis might be the basis for an elegant general method of determining (or at least, approximately checking) monomer reactivity ratios. The pyrolysis of samples of (V) of known composition may therefore be regarded as a test of the practicability of this method.

If chain depolymerisation of (IV) starts at the loose poly(methyl α-methylacrylate) chain ends, and stops at the first attachment to a

polyester chain, as was tentatively suggested by Mackinnon,[55] a systematic study of this process could possibly yield information on the mean length of the loose ends of the polyaddition chains in the network, and, indirectly, on the average length of the polyaddition chain segments acting as cross-links. Some confirmation of the monomer reactivity ratios governing the cross-linking of (IV) could thus be obtained.

A study of the degradation characteristics of (V) could clearly give an indication of the value of undertaking the latter project.

2. DISCUSSION OF RESULTS

2.1 The Pyrolysis of Poly(diethyl maleate-methyl α-methylacrylate)(V).

General Preliminary Considerations

The molar ratio of methyl α-methylacrylate to diethyl maleate in the copolymer (V) prepared as described in the Experimental Section, was ca. 18:1. The number-average molecular weight (Mn) was found osmotically to be ca. 471,000.

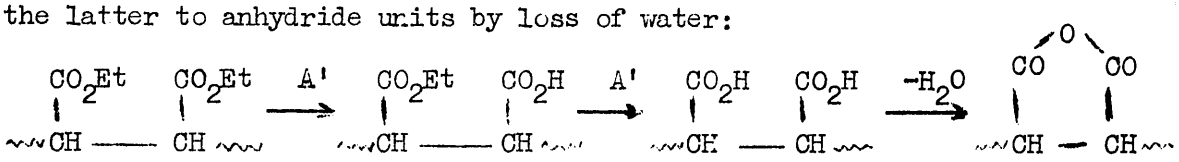
Temperature of Pyrolysis

Before studying the thermal degradation characteristics of (V), a suitable temperature for pyrolysis was first determined. The lower temperature limit is, of course, the onset temperature of degradation. As noted by Grassie[96], however, when poly(methyl α-methylacrylate) is pyrolysed below 160°, the characteristics of thermal degradation are complicated by secondary effects arising from the slow rate of diffusion of monomer through the highly viscous polymer.

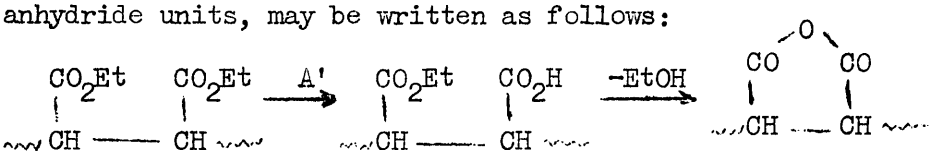
The onset temperature of pyrolysis of (V) was found to be 170°. More precisely, this is the lowest temperature at which a detectable amount of unsaturated product, presumably methyl α-methylacrylate, was evolved from the copolymer in the onset-temperature determination apparatus described in the Experimental Section (p.126).

The upper limit of temperature for the pyrolysis of (V) is the onset temperature for A' scission of the carbethoxy groups in the copolymer. The carbomethoxy groups are, of course, stable up to higher temperatures (see p. 127). The onset temperature for A' scission of (V) was found to be 280° (which is considerably lower than that of the relatively simple

ester, diethyl succinate, for which breakdown by A' scission commences at 330° [55]. Pyrolysis of (V) at temperatures above 280° would probably be complicated by structural changes in the copolymer, resulting from the thermal conversion of carbethoxy groups to carboxylic acid groups, and of the latter to anhydride units by loss of water:



An alternative sequence of reactions, also leading to formation of anhydride units, may be written as follows:



An analogous sequence was postulated by Brown[98] to explain the detection of ethanol and succinic anhydride in the pyrolysate from diethyl succinate.

The intramolecular formation of anhydride units which occurs during the thermal degradation of poly(tert.-butyl α-methylacrylate) has been shown by Grant and Grassie[99] to have a marked inhibitory effect on the depolymerisation of the polymeric residue.

The pyrolysis of (V) was therefore studied well within the limits 170 - 280°, at 220° and 260° respectively.

Prevention of oxidation and catalysis

To avoid oxidation, (V) was pyrolysed under high vacuum, a technique which also facilitates rapid removal of volatile products from the reaction zone and thus prevents possible secondary reactions.

In the thermal degradation of poly(methyl α-methylacrylate) at 220°, Grassie and Melville[86] used copper powder in intimate contact with the molten polymer to improve heat transfer without apparent catalytic effect. Copper is nevertheless known to have catalytic influence in many free-radical reactions. Kern et al[100] have recently reported that when polymerisation of methyl α-methylacrylate is completed between copper sheets, small amounts of copper may be detected some distance within the polymer mass. To explain this, it was suggested that the copper formed a complex which then migrated through the polymer mass. It is considered probable that such complex formation will be favoured at the high temperatures encountered in pyrolysis, when both monomer and polymer are present. No matter how efficient the removal of monomer from the pyrolysis system in vacuo, there will always be a small amount present in the degrading polymer as a result of diffusion.

To minimise possible catalytic side-reactions, therefore, an all-Pyrex glass reaction vessel was used in the present work.

Approach to the Problem

Since the complete kinetic analysis of the thermal degradation of a copolymer is inevitably much more complex than that of a simple homopolymer, attention has been centred on the molecular weight changes which accompany the pyrolysis of (V) rather than on kinetic measurements. In addition, however, very approximate measurements of volatilization rate at each temperature (220° and 260°) have been made, by interpolating the loss-in-weight data observed for a series of pyrolyses of varying duration.

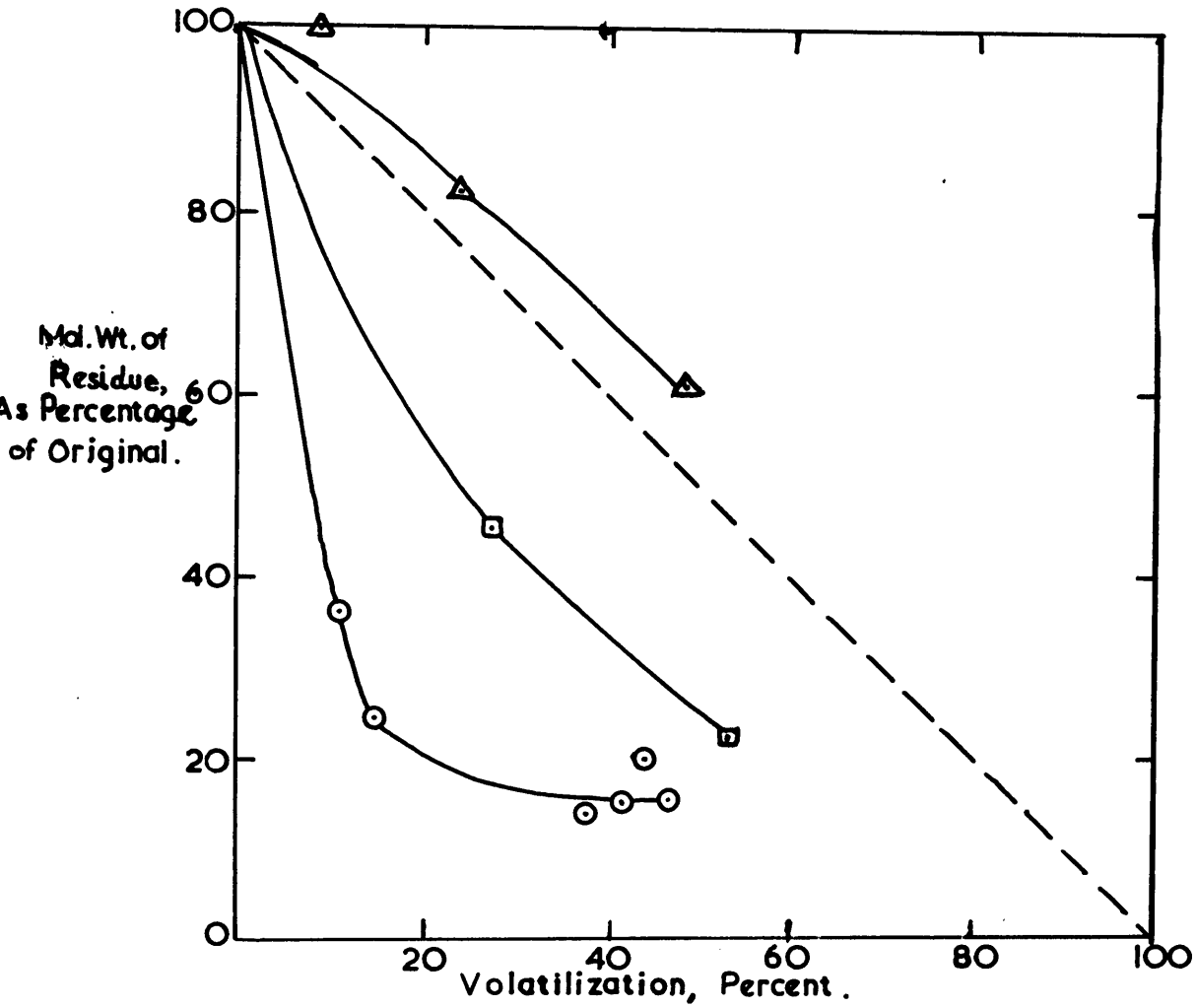


FIGURE 5.

Experimental Curves Observed for Thermal Degradation of

△ Poly (methyl α-methylacrylate), Pyrolysed at 260° ;
⊙ Poly (diethyl maleate-methyl α-methylacrylate), Pyrolysed at 260° ;
⊡ Poly (diethyl maleate-methyl α-methylacrylate), Pyrolysed at 220° .

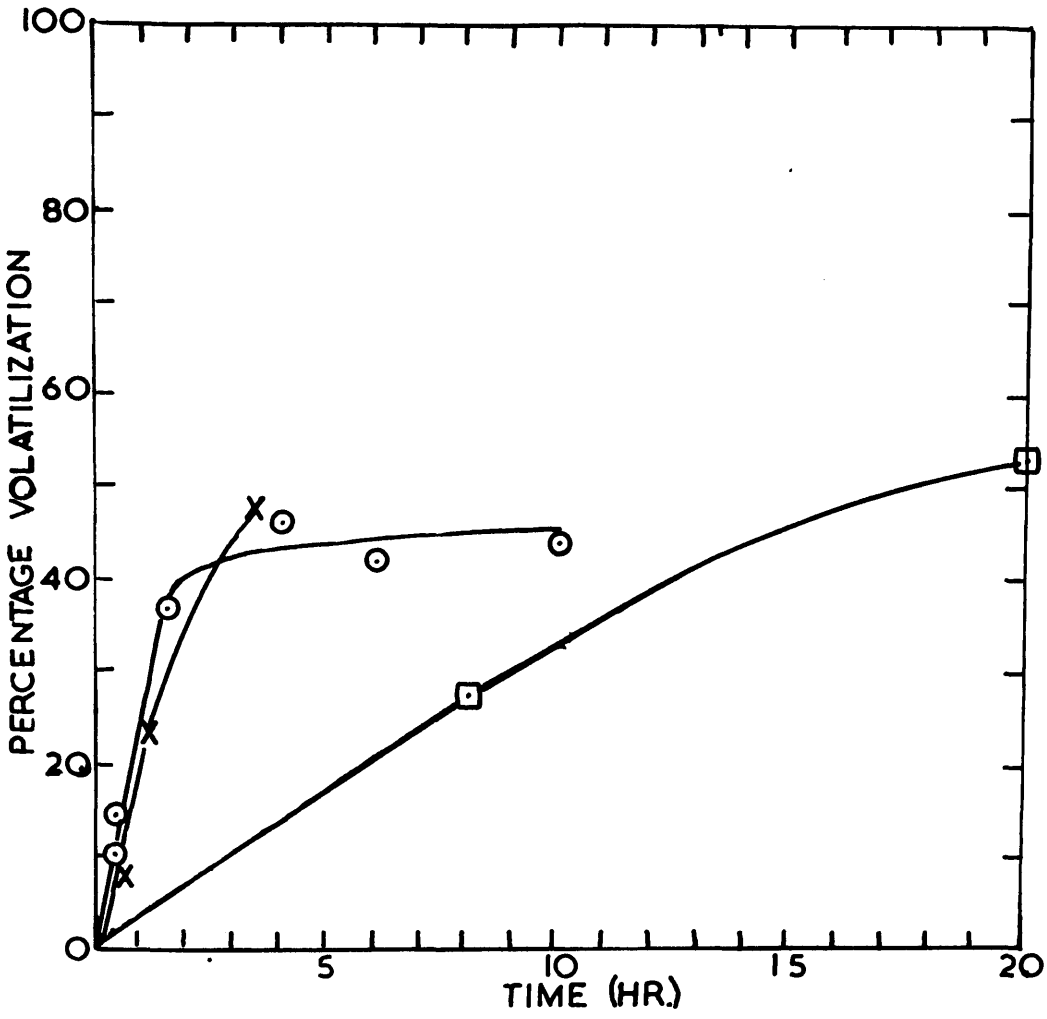


FIGURE 6.

EXPERIMENTAL CURVES OBSERVED FOR PYROLYSIS OF

X Poly(methyl α-methylacrylate), at 260° ;

⊙ Poly(diethyl maleate-methyl α-methylacrylate) at 260° ;

⊡ Poly(diethyl maleate-methyl α-methylacrylate) at 220° .

2.2 Pyrolysis Characteristics

The general conditions and results of pyrolysis of (V) and related substances are summarized in Table 3 (in Experimental Section of Part II).

Specimens of (V) were pyrolysed for various lengths of time at 260° (Runs 1 - 6) and at 220° (Runs 7 and 8). From the graph of relative number-average molecular weight against percentage volatilization, (Fig. 5 : lowest curve) it is apparent that the thermal degradation of (V) at 260° proceeds with a sharp initial fall in molecular weight, which gradually levels off to ca.15% of the original value at ca.45% conversion, when degradation stops. A similar though less marked decrease in molecular weight is observed for pyrolysis at 220° (middle curve). The uppermost curve is that observed for a reference sample of poly(methyl α-methylacrylate) ($\overline{M}_n$ = 717,000), pyrolysed (Runs 9 - 11) under the same experimental conditions as for (V), at 260°.

Fig. 6 shows that the initial rate of volatilization of (V) at 260° is slightly higher than that for poly(methyl α-methylacrylate). Volatilization of (V) at 220° is, on the other hand, slow compared with that at 260°. For all three pyrolyses, its rate fell to zero after ca.40 - 50% conversion.

The volatile products of pyrolysis of (V) at 220° and at 260° were identified by vapour phase chromatography as methyl α-methylacrylate (major product), diethyl maleate (minor product), and diethyl fumarate (minor product). As expected, only methyl α-methylacrylate could be

detected in the volatile pyrolysate from poly(methyl α-methylacrylate).

The gradual fall in molecular weight of the poly(methyl α-methylacrylate) sample during degradation at 260° is best explained as the result of disproportionation termination of pairs of degrading radicals: a similar result has been observed by Grassie and Melville[86] for the pyrolysis at 220° of samples of poly(methyl α-methylacrylate) of Mn higher than ca. 500,000.

Moreover for poly(methyl α-methylacrylate) samples which contain equal numbers of terminally saturated and unsaturated molecules, Mn cannot theoretically fall below 50% of the original value if disproportionation is the sole cause of decrease in molecular weight. Since the number-average molecular weight of (V) fell to ca. 15% of the original after pyrolysis at 220-260°, it might therefore be deduced that chain scission occurs, followed by depolymerisation of the resulting fragments, a process comparable with the pyrolysis at 220° of poly(acrylonitrile - methyl α-methylacrylate).[86] If, however, chain scission were to take place at every diethyl maleate unit in the 18:1 copolymer, of Mn = 471,000, a simple calculation shows that the molecular weight of the latter would fall to ca. $\frac{1}{260}$ th. of its original value - far below the experimentally observed limiting value of ca. $\frac{1}{7}$ th.

Since, moreover, the residual copolymer showed no further decrease in molecular weight on prolonged heating at 260° for 5 hr. after volatilization had ceased (Run 1), it follows that the diethyl maleate linkages in (V) are not inherently unstable at that temperature. Weak links which could conceivably be present in limited number are those which might arise

by incorporation of molecular oxygen (or other impurity) into the copolymer during copolymerisation. Nevertheless, the experimental conditions of copolymerisation, in particular the use of high vacuum and purification of the monomers and catalyst, were such as to eliminate impurities: weak links in the copolymer are therefore considered unlikely. Further proof of the inherent thermal stability at 220° of the diethyl maleate units in (V) and of the absence of weak links is given below.

2.2.1 Site of Initiation of Degradation of (V)

From the apparent thermal stability of the diethyl maleate linkages in (V) it might be inferred that the initiation of the thermal degradation of (V) at 220° and at 260° occurs in the vicinity of the chain-ends, perhaps with formation of free radicals, as for poly(methyl α-methylacrylate) pyrolysed below 300°.

To test this idea, attempts were made to inhibit degradation by pyrolysing the copolymer in the presence of various known free radical inhibitors (Runs 12-16). Most of the common organic free radical inhibitors, such as the anthraquinone dyestuffs, were too volatile at 260° for this purpose. Even 1:4 -diaminoanthraquinone, successfully used by Grassie and Melville[86] to inhibit completely the degradation at 220° of poly (methyl α-methylacrylate), was found to be too volatile at 260°.

Addition of fine copper powder (ca. 25% w/w) to (V) failed to produce any marked inhibition at 260°, as is apparent from comparison of the results of Run 2 and Run 12.

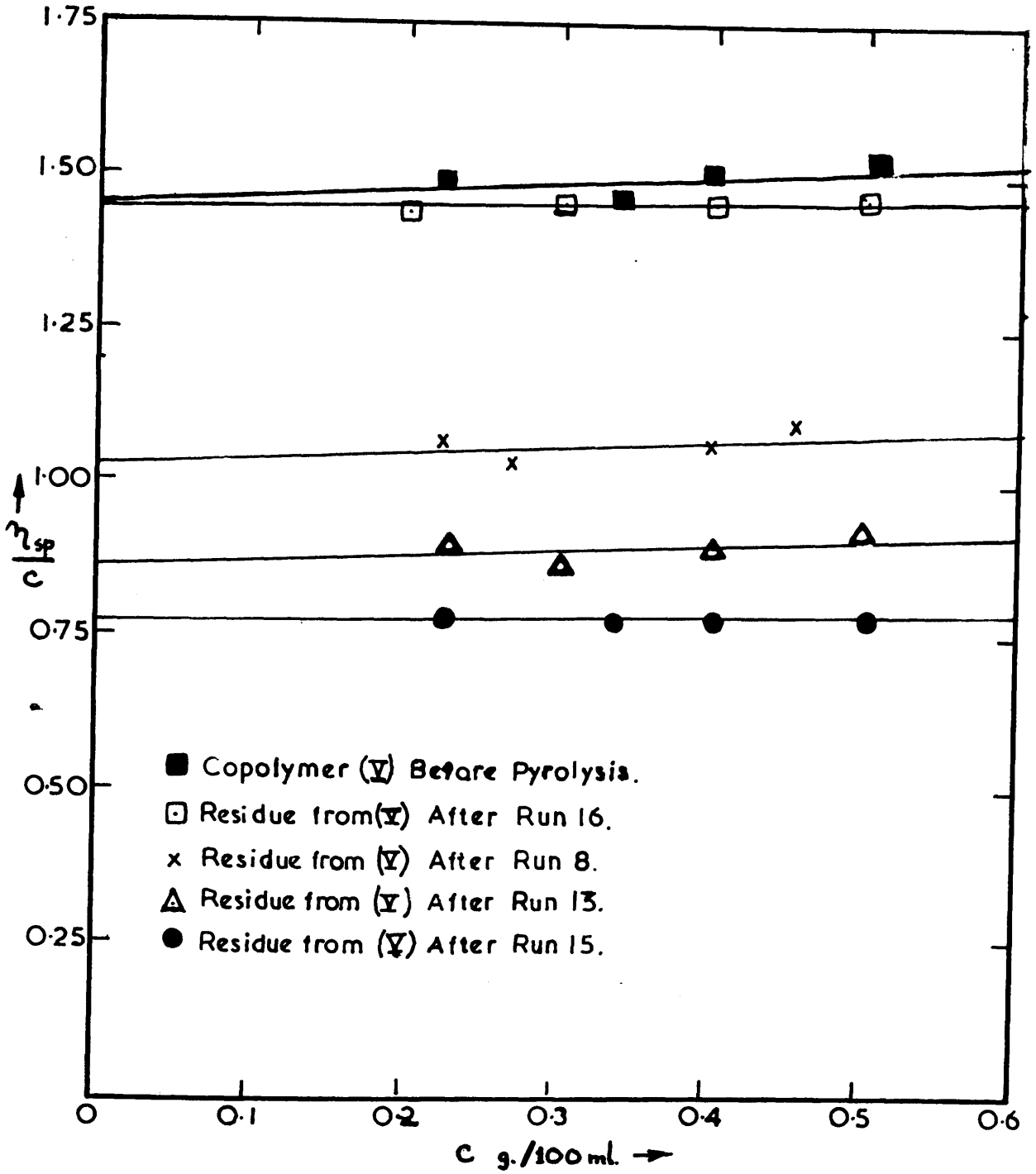
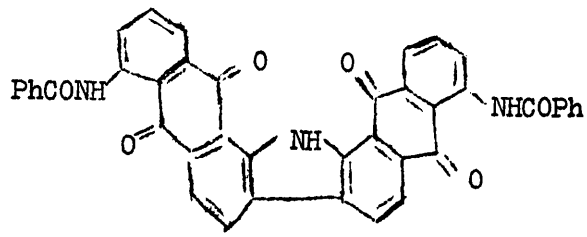


FIGURE 7.

Intrinsic Viscosities in Benzene Solution at 20°C.

Pyrolysed alone at 260° for a period of 1.5 hrs. (Run 3), (V) undergoes ca. 37.6% volatilization. Addition of ca. 2% w/w of the involatile dyestuff 'Caledon Gold Orange 3G', of formula:



to (V) before pyrolysis under the same conditions reduced volatilization to 10.5% (Run 13). In an analogous experiment (Run 14) addition of ca. 2% w/w of 1:4-dibenzamidoanthraquinone reduced volatilization to 27%.

The number-average molecular weight of the polymeric residue remaining after degradation in the presence of an added inhibitor cannot be accurately measured by the osmotic method, since traces of the relatively low molecular weight inhibitor would give rise to an osmotic pressure, and probably also affect the semipermeable membrane. Measurements of intrinsic viscosity were therefore used to indicate molecular weight changes, since this method is insensitive to traces of inhibitor. Viscosimetric data show that the molecular weight of (V) pyrolysed at 260° in presence of the most effective inhibitor tried ('Caledon Gold Orange 3G': Run 13) still fell considerably below the original value.

Since no highly efficient inhibitor could be found for the reaction at 260°, and the molecular weight of the residual copolymer rapidly falls

to a low value after only a few percent degradation, no definite conclusions could be reached about the site of initiation at that temperature. It is nevertheless obvious that the reaction is free-radical in character, since it is retarded to a certain extent by small amounts of the substances tried.

To study the reaction at lower temperatures, equimolar amounts of 1:4-diaminoanthraquinone and (V) were heated together at 220° for 17 hours (Run 15), during which time 32.3% volatilization occurred [cf. 53.5% volatilization when (V) is pyrolysed alone at 220° for 20 hrs (Run 7)]. On increasing the amount of inhibitor to 2% w/w, however, which represents a large molar excess of inhibitor to (V), complete inhibition of degradation was observed on prolonged heating for 9 hours at 220° (Run 16). The molecular weight of the copolymer was found viscosimetrically to have undergone no change during this period. This is in marked contrast with the pyrolysis of (V) alone at 220° for 9 hours (Run 8) when 27.5% volatilization occurred and the molecular weight fell to 44.3% of original.

The function of the inhibitor is to react with and stabilize free radicals formed in the system and thus prevent their participation in chain reactions such as depolymerisation. The inhibitor cannot prevent the initial formation of these radicals, but merely reacts with them once they have been formed. If scission to a pair of free-radicals were to occur near the middle of each chain, there would be a marked fall in molecular weight. If scission occurred in the region of the chain-ends, on the other hand, the molecular weight of the residue would remain essentially constant. It follows, therefore, that the free-radical initiation

of degradation of (V) at 220° occurs at or near the chain-ends. This result also demonstrates that at 220° there are no thermally weak linkages in the copolymer chain backbone. Although rigid proof is lacking it is probable that the same initiation mechanism also holds at 260°, since random scission of the carbon-carbon bonds in the chain backbone of vinyl polymers does not normally occur below 300°. A similar result was observed by Grassie and Melville[86] for the inhibition of degradation of poly(methyl α-methylacrylate) at 220° by small amounts of 1:4-diaminoanthraquinone.

2.2.2 The Macromolecular Structure of (V)

(a) Chain-end structures

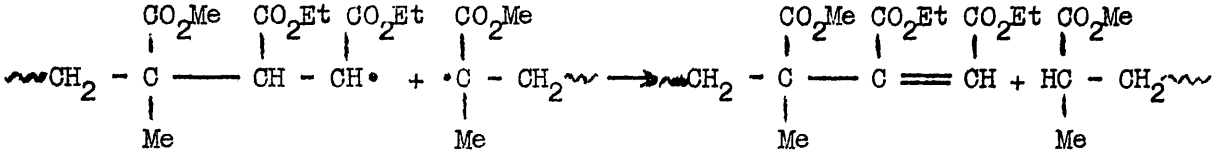
Under the experimental conditions of copolymerisation employed (benzoyl peroxide (0.1 mols%) as initiator at 60°) it may be reasonably assumed that every growing radical in the copolymerisation system contains an initiator fragment at one end. In the homopolymerisation of vinyl monomers, chain termination of growing free radicals generally occurs either by disproportionation or combination of pairs of radicals. There are three reasons for believing that cross-disproportionation is likely to be an important chain-termination process in the copolymerisation of methyl α-methylacrylate and diethyl maleate at 60°.

(i) At 60°, the homopolymerisation of methyl α-methylacrylate is known[90] to be terminated entirely by disproporationation of pairs of growing radicals;

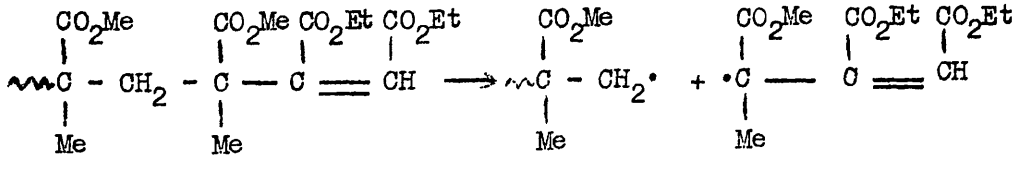
(ii) Cross-termination is known to be markedly favoured in nearly all copolymerisation systems;[101]

and (iii) The penultimate tertiary hydrogen atom of a diethyl maleate-type macroradical should be even more readily transferred in an act of disproportionation than the penultimate methylene hydrogen atom of a methyl α-methylacrylate-type macroradical.

The mechanism proposed for chain termination by disproportionation is therefore as shown:



For benzoyl peroxide-catalysed poly(methyl α-methylacrylate) samples, the initiator fragment at one end of each molecule has been shown[86] to be stable to at least 220°. The saturated end formed in disproportionation termination is similarly stable; the unsaturated end thus formed, however, is capable of initiating depolymerisation at 220° by splitting into two fragments - a relatively stable allyl-type radical and an unstable macroradical which immediately depolymerises. A similar degradation initiation mechanism can be proposed for the terminally unsaturated molecules of (V) formed during copolymerisation:



Termination of copolymerisation by combination of a growing methyl α-methylacrylate-type macroradical with a diethyl maleate-type macroradical

can, of course, also possibly occur. The suggestion that approach of these two radical-ends might be disfavoured sterically is refuted in view of the structural symmetry of diethyl maleate and the obvious fact that copolymerisation with methyl α-methylacrylate does occur.

There is, indeed, experimental evidence to suggest that the termination of copolymerisation of diethyl maleate and methyl α-methylacrylate occurs by simultaneous cross-combination and cross-disproportionation. Melville et al.[102] have shown that the characteristic values of $\frac{Mw}{Mn}$ (i.e. the ratio of weight-average to number-average molecular weight) are theoretically the same for copolymerisation as for homopolymerisation: in either process, termination entirely by combination results in a $\frac{Mw}{Mn}$ ratio of 1.5, while termination entirely by disproportionation gives a ratio of 2.0. Mw and Mn were measured for the undegraded sample of (V) by the osmotic and light-scattering methods respectively. Respective values of 828,000 and 471,000 were observed, giving a $\frac{Mw}{Mn}$ ratio of 1.76. This value, lying close to the arithmetic mean of 1.5 and 2.0, suggests that termination of the copolymerisation of methyl α-methylacrylate and diethyl maleate at 60° may occur by combination and disproportionation to an approximately equal extent.

It follows that the weight fraction of molecules bearing unsaturated chain-ends in the copolymer should be theoretically ca. 25%. If chain-end initiated depolymerisation were the only molecular weight-reducing process in the degradation of (V), a simple calculation shows that the number-average molecular weight cannot fall below ca. 75% of the original

value, and a theoretical maximum of only ca. 25% volatilization can occur.

It was observed experimentally, however, that the number-average molecular weight of the copolymer pyrolysed at 260° fell to ca. 15% of the original value, and that ca. 50% volatilization occurred. Clearly, then, molecular weight-reducing processes other than chain-end initiated depolymerisation must take part in the pyrolysis of (V) at 260°.

(b) Possibility of Branching in (V)

The failure of an equimolar amount of 1:4-diaminoanthraquinone to inhibit completely the degradation of (V) at 220° might suggest that there is a far greater average number of terminal double bonds per copolymer molecule than was originally supposed. The possibility of chain branching of the copolymer must therefore be considered. This could have the effect of producing on a given copolymer molecule a number of chain-ends, a fraction of which are unsaturated. The complete inhibition of degradation observed on adding a large molar excess of inhibitor to the copolymer before pyrolysis at 220° would appear to suppor this theory.

Stockmayer and Fixman[103] have developed a general method for determining the degree of branching of polymers by viscosity measurements. According to their theory.

$$k_3 = \frac{[\eta]_{branched}}{[\eta]_{linear}}$$

where k_3 is the ratio of the effective hydrodynamic radius of a branched polymer molecule to that of a linear molecule of the same weight-average

molecular weight,

$[\eta]_{branched}$ is the intrinsic viscosity of the branched sample,

and $[\eta]_{linear}$ is the intrinsic viscosity of a linear sample of the same weight-average molecular weight and local chain structure as the branched sample.

λ^3 has been plotted against the theoretical number of trifunctional branch-points per polymer molecule.[104] To determine the degree of branching, the intrinsic viscosity-weight-average molecular weight relationship must be known for the linear polymer of the same local chain structure as the branched sample.

$[\eta]_{branched}$ and Mw are measured for the branched polymer and the value of $[\eta]_{linear}$ calculated for the same Mw as the branched sample. Hence λ^3 is calculated, and the number of branch points per molecule simply read from the theoretical curve referred to above.

Assuming that (V) is branched, its $[\eta]_{branched}$ and Mw were readily measured. Precise evaluation of $[\eta]_{linear}$ for the copolymer could not be achieved, however, since a definitely linear sample of the copolymer was unobtainable. As a first approximation, it was therefore assumed that the intrinsic viscosity - weight-average molecular weight relationship is the same for the linear 18:1 copolymer as for linear poly(methyl α-methylacrylate). Substituting the values of Meyerhoff and Schulz[105] for K and α in the equation,

$$[\eta] = K' M_w^{\alpha}$$

where K' and α are constants for the polymer-solvent system and $[\eta]$ and Mw have their usual significance,

we have, for the 18:1 copolymer

$$[\eta]_{\text{linear}} = 0.84 \times 10^{-4} \times 828{,}000^{0.73}$$
$$= 1.77$$
$$\text{and } h^3 = \frac{1.46}{1.77} = 0.82$$

Hence, from the theoretical curve, the approximate average number of branch points per molecule of (V) was found to be 1.8. Considering the approximations made, however, it can only be concluded that there is possibly a low degree of branching in the copolymer.

(c) Possible Mechanism of Chain Branching during Copolymerisation

In the bulk homopolymerisation of vinyl monomers, there are two widely recognised ways in which branching may occur. Each of these depends on a chain transfer process, one with monomer, the other with previously-formed polymer.

A growing macroradical can undergo chain transfer by abstracting a labile hydrogen atom from a monomer molecule. This results in formation of a polymer bearing a terminal unsaturated group which may be combined as one of the units entering into the subsequent growth of another polymer molecule. A polymer molecule with a single branch is thus formed. Repetition of this process with addition of the terminal unsaturated groups of several polymer molecules can clearly lead to formation of highly branched structures.

A growing macroradical may undergo chain transfer with polymer by abstracting a hydrogen atom (usually tertiary) from the chain backbone, leaving behind a free radical which can then generate a branch by the

addition of successive monomer units. Chain transfer with polymer is a more efficient branching process than transfer with monomer, since every act of transfer results directly in the formation of a branch.

Poly(vinyl acetate), polymerised to high conversion,[85] is an example of a polymer with branches formed partially by chain transfer with monomer (the hydrogen atoms of the acetoxy group being sufficiently reactive for transfer) and partially by transfer with polymer (by removal of tertiary hydrogen atoms attached to the polymer chain backbone).

Methyl acrylate, on the other hand, undergoes branching on polymerisation chiefly by chain transfer to polymer.[84]

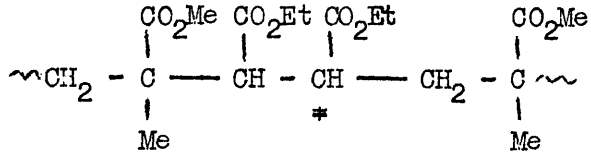
Since every branch-forming act of transfer yields one branch and two chain ends, and there will ordinarily be other chain-ends in a polymerisation system, formed, e.g. in initiation and termination, it follows that the ratio of branch points to chain ends (α) cannot exceed the critical value 0.5 in absence of reactions other than those just considered.

As shown by Fox and Gratch,[84] however, if termination in such a system occurs predominantly by combination of pairs of growing radicals, the proportion of chain-ends is reduced, and α may exceed 0.5. Since cross-linking occurs if two branch radicals combine, and a given molecule may contain more than one branch, it is apparent that polymerisation by such a mechanism may lead to gelation.

Gelation of poly(vinyl acetate) occurs at very high conversions.[85]

Methyl acrylate, polymerised in bulk, readily undergoes microgelation at conversions less than 1%, to the well-known 'popcorn' type of polymer.[84] No gelation has been observed, however, for the bulk homopolymerisation of other common monomers, such as methyl α-methylacrylate or styrene.

In (V), each maleate unit contains two tertiary hydrogen atoms that are theoretically capable of removal by chain transfer:



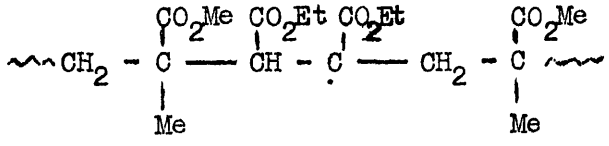
Sterically, the more vulnerable of the two would appear to be the one marked *. During copolymerisation, a growing macroradical could approach and abstract this hydrogen atom more easily than the other, leaving behind on the copolymer backbone a free radical capable of initiating a branch.

The possibility of chain transfer with each monomer during copolymerisation must also be considered. Since transfer with monomer is unimportant in the bulk polymerisation of methyl α-methylacrylate, it is assumed to be so in copolymerisation also. Although it is difficult to exclude with certainty the possibility of chain transfer with diethyl maleate (its participation in chain transfer reactions has not hitherto been recorded), its slight structural similarity to ethyl acrylate would suggest that chain transfer to this monomer is also unimportant (acrylic esters do not generally exhibit chain transfer to monomer in polymerisation).

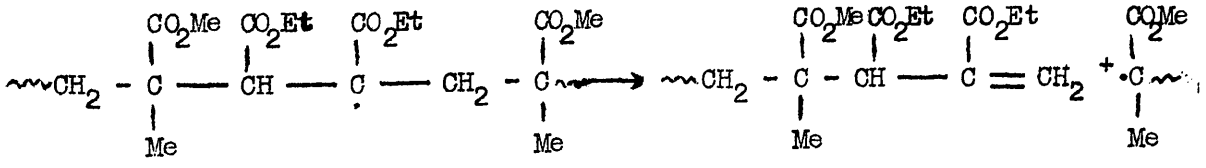
Summarizing, it would appear that chain transfer to copolymer is the most likely possible source of branching for (V). Although combination of free radicals plays a considerable part in chain termination during copolymerisation, the degree of branching was apparently too low to produce gelation.

(d) Possible Influence of Branching on the Degradation of (V)

Although the overall average degree of branching of (V) is very low, branching may have a profound effect on the pyrolytic behaviour of a given branched copolymer molecule. If degradation from the end of a terminally unsaturated branch proceeds as far as the point on the chain backbone where the branch originated, a tertiary free radical is formed:

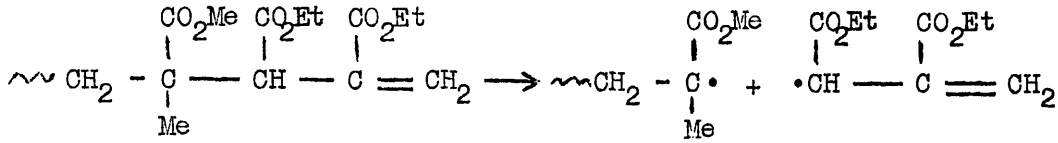


This radical is identical with the one formed during copolymerisation by chain transfer to copolymer. Under the degradative conditions at 220 - 260°, it is probable that this radical splits into a shorter free radical and a relatively stable unsaturated chain-end:

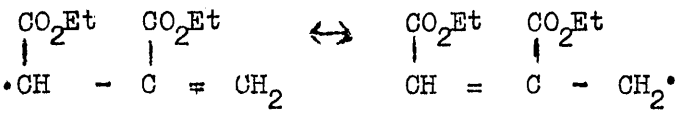


A similar mechanism has been proposed by Oakes and Richards[106] for one of the principal routes of pyrolysis of polyethylene. Depolymerisation of the shorter radical formed can, of course, occur immediately. The unsaturated

chain-end can eventually undergo homolytic scission to an allyl-type radical and a macroradical which immediately depolymerises:



The allyl-type radical thus formed is identical (by virtue of resonance) to the one generated in initiation of degradation by the mechanism proposed above:



Because of the extremely small number of these allyl-type radicals formed in the system, however, it is impossible to determine their fate. Complete depolymerisation of a branch can thus result in chain scission of the copolymer at the original trifunctional branch point, with the further possibility of chain depolymerisation in both directions away from the site of the break. This process, if it occurred widely, could partly account for the initial fall in the number-average molecular weight of (V) observed during its pyrolysis at 220 - 260°.

2.3 Influence of Molecular Weight Distribution on the Degradation of (V)

As pointed out by Grassie[96], the characteristic degradation curve of molecular weight as a percentage of the original versus percentage volatilization for an unfractionated polymer sample is the net result of two processes. These are

(i) Total elimination of the smaller molecules by their rapid and complete depolymerisation,

and (ii) Partial degradation of those larger molecules for which the kinetic chain length of depolymerisation is less than the degree of polymerisation.

Of these processes, (i), tends to increase the number-average molecular weight of the residual polymer, whereas (ii) tends to reduce it.

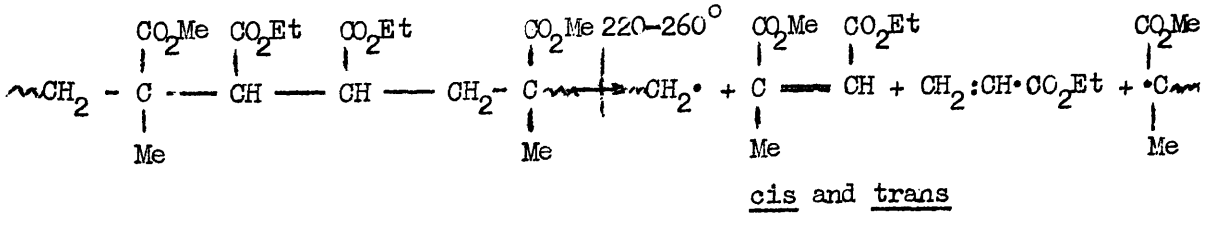
The molecular weight distribution of a polymer formed over a finite range of conversion is the summation of that of increments made under different conditions. The distribution of the polymer being formed over a small range of conversion can be calculated without great difficulty. As conditions change with increasing conversion, however, the overall molecular weight distribution broadens somewhat, and, if branching occurs, extremely broad molecular weight distributions can result. The great breadth arises from the fact that each act of chain transfer to polymer adds a branch to the molecule, increasing its molecular weight. Since the probability of branching is approximately proportional to the weight-average molecular weight, branched molecules tend to become more and more highly branched, as a result of which the molecular weight distribution curve has a long, high molecular weight 'tail'. For branched polymers, the ratio $\frac{\overline{Mw}}{\overline{Mn}}$ may become very much higher than for the corresponding linear polymers. Highly branched polyethylene, for example, may have a $\frac{\overline{Mw}}{\overline{Mn}}$ ratio as high as 50[107]; for this polymer, moreover, it was also found that there is a very broad distribution in the number of branches per molecule, a large fraction of the molecules remaining unbranched.

Applying these considerations to (V), it is apparent from the low $\frac{Mw}{Mn}$ ratio of 1.76 that no measurable broadening of the molecular weight distribution has occurred - a result in good qualitative agreement with the very low degree of branching estimated viscosimetrically.

The low conversion (ca.10%) at which copolymerisation was arrested is no doubt mainly responsible for this. It follows that the effects of branching on the molecular weight distribution of (V), and consequently on the shape of the characteristic degradation curve (Fig. 5) are, at most, very slight.

2.4 Chain Depolymerisation of (V)

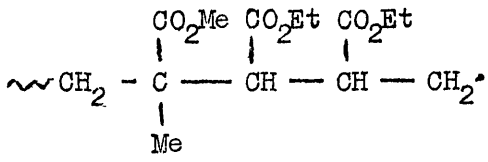
The volatile products of degradation of (V) at 220 - 260° have been shown by vapour-phase chromatography (Experimental Section: Fig.12) to consist of methyl α-methylacrylate (major product), diethyl maleate (minor product) and diethyl fumarate (minor product). This shows that direct chain depolymerisation is an important process in the degradation of (V) under the experimental conditions employed. No hybrid monomer effect was observed: ethyl acrylate and the mixed methyl ethyl esters of mesaconic and citraconic acids could not be detected in the pyrolysate from (V).



The geometric isomerism displayed by diethyl maleate and diethyl fumarate is, of course, lost when either is incorporated into a copolymer, by opening of the double bonds and free rotation about the newly-formed

C-C single bonds within the copolymer chain backbone. Depolymerisation of such a copolymer may formally yield either the maleic or fumaric ester. This qualitatively explains the detection of both isomeric products in the pyrolysate from (V). Similarly, both isomers were identified as minor products in the pyrolysate from a copolymer of diethyl fumarate and methyl α-methylacrylate, pyrolysed at 260° (Run 17) under the same conditions as for (V).

Since thermal initiation of the depolymerisation of (V), according to the mechanism proposed above, occurs by the splitting-off of an allyl-type radical from an unsaturated chain end, the degrading macroradical thus formed, after splitting off successive methyl α-methylacrylate units, will almost certainly yield the intermediate structure shown:



This macroradical may then theoretically either (i) split off successively ethyl acrylate and methyl ethyl mesaconate or citraconate, followed by elimination of a series of methyl α-methylacrylate units; or (ii) split off a methylene diradical, followed by elimination of diethyl maleate or fumarate and a series of methyl α-methylacrylate units; or (iii) abstract a hydrogen atom by transfer or termination and thus form a stable end-structure.

Of these possibilities, process (i) would be expected to lead to a strong hybrid monomer effect, since it could theoretically be repeated

all along the depolymerising copolymer chain. Process (ii), on the other hand , is considered to be much more likely. Since it accounts for the experimentally observed products. No products could be detected in the pyrolysate from (V) which might indicate the existence of a hybrid monomer effect at 220-260°.

This experimental observation is in agreement with the general conclusions of Wall,[94] who recorded that the pyrolysis of copolymers of methyl α-methylacrylate, even at relatively high temperatures (ca. 425°), is not accompanied by formation of hybrid monomers.

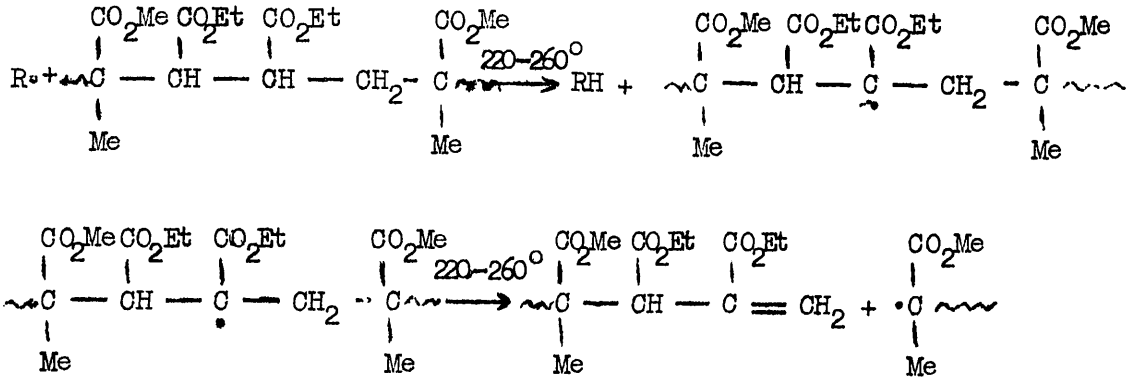
The formation of only one methylene diradical per degrading copolymer chain is thus sufficient to account for the observed products. The fate of the methylene diradicals so formed is unknown, but it is highly probable that they would combine in pairs to form ethylene (cf. combination of methylene diradicals in the A° scission of methyl acetate[7]).

Process (iii) comes into the category of chain transfer or chain termination, and is discussed in the appropriate sub-sections (see below).

2.5 Chain Transfer in the Degradation of (V)

An important feature of the pyrolysis of (V) at 220-260° is the possibility of intermolecular chain transfer. A degrading macroradical in the system might abstract a tertiary hydrogen atom from the copolymer chain backbone, leaving there a tertiary tree radical. Since this radical is identical with the one formed by complete depolymerisation of a branch (see above) it follows that every act of transfer at 220-260° should

result in chain scission of the copolymer at the point attacked:



Thus chain transfer at 220-260° may introduce a considerable degree of randomness into the overall thermal degradation process. As seen from Fig. 5, the initial fall in molecular weight is steeper at 260° than at 220°. This is attributed to a greater degree of chain transfer at 260°, since transfer is, in general, favoured by high temperatures. Since the molecular weight of the degraded copolymer at 260° reached a limiting value of ca. 15% of the original, it is apparent that chain transfer can only have occurred at a small fraction of the total number of tertiary hydrogen atoms available.

From the sharp initial fall in molecular weight observed at 260° (Fig. 5) it is probable that several acts of transfer occur for every kinetic chain initiated at that temperature.

According to the overall chain transfer scheme proposed above, two degradable chain-ends should result from one originally present: the terminal double bond formed by chain scission after transfer may, under the prevailing degradative conditions, eventually react to form

a depolymerising chain-end. If this is correct, transfer should strongly promote volatilization, since the cumulative effect of successive transfer acts should be to increase the rate of initiation and also the ultimate extent of volatilization. The approximate rate measurements made (Fig. 6) do not, however, permit detection of any rate increase that may have occurred.

At 220° and at 260°, volatilization of (V) occurred to the extent of ca.50%, which is approximately equal to that of the reference specimen of poly(methyl α-methylacrylate) pyrolysed under the same conditions at 260°. For the homopolymer, this is the expected result, since 50% of the polymer molecules theoretically possess a terminal double bond. Theoretically only ca. 25% of the molecules in the sample of (V) pyrolysed were terminally unsaturated, however, so that transfer appears to have doubled the extent of volatilization that would otherwise have occurred.

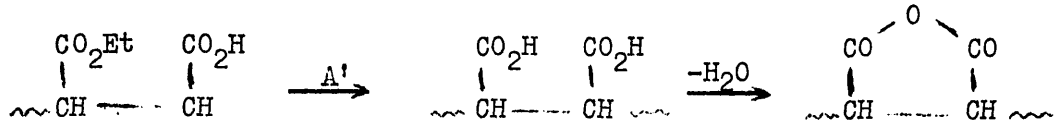
It is apparent from Fig. 5 that the effect of increased transfer at 260° in sharply reducing the molecular weight of the copolymer is not accompanied by a corresponding increase in the extent of volatilization relative to that observed at 220°. It can only be supposed that some stabilized structure is produced which prevents complete depolymerisation from the reactive chain-ends formed by chain scission after every act of transfer.

The mechanism of formation of such a structure is, however, uncertain. I^+ might be thought to be a catalytic effect, associated in some

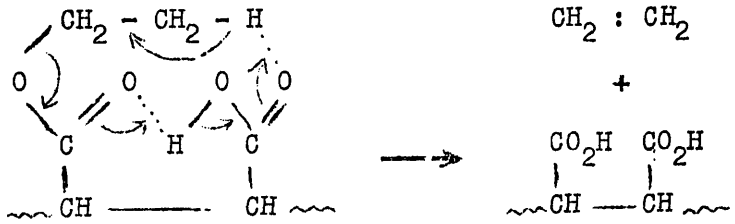
way with the unexplained progressive development of a brownish coloration observed throughout pyrolysis of (V) at 220-260°, this being more pronounced at the higher temperature: the catalytic effects of carbonization have already been referred to in the Introduction to Part I of this thesis. A more likely explanation, however, is the pyrolytic formation of occasional anhydride groups along the copolymer chain, these having a marked inhibitory influence on depolymerisation.[99] Close examination of the vapour-phase chromatogram of the diethyl maleate sample used in the preparation of (V). (Fig. 12a)reveals the presence of two tiny peaks, corresponding to traces of unidentified impurities, together with a small hump corresponding (Fig. 12 b) to a trace of diethyl fumarate. The presence of diethyl fumarate is best attributed to slight thermal isomerisation of maleic to fumaric diester during esterification or fractionation. One of the two unidentified impurities present in the sample of diethyl maleate might be monoethyl maleate, formed either by incomplete esterification or (as is more probable) by a slight degree of A' scission during subsequent fractional distillation of the product.

Unfortunately, a specimen of the mono-ester was not available for use as a standard for vapour-phase chromatography - its b.p. and other physical constants do not appear to have been recorded in the literature. Maleic acid, maleic anhydride or fumaric acid, each of which might conceivably be present as an impurity, could not be detected in the sample of diethyl maleate by vapour phase chromatography.

If occasional monoethyl maleate units were incorporated into (V) during copolymerisation, each of these could have the effect of promoting pyrolytic A' scission of the adjacent carbethoxy group, followed by formation of a 5-membered cyclic anhydride group by loss of water from the resultant adjacent carboxylic acid units:



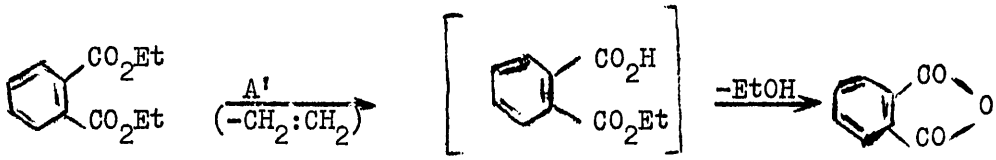
A similar mechanism has been proposed by Grant and Grassie[99] for the intramolecular formation of anhydride units within the polymer chain during the thermal degradation of poly (tert - butyl α-methylacrylate). Proximity of a carboxylic acid unit was shown to facilitate A' scission of ester groups attached to the chain. The mechanism now proposed for (V) is as follows:



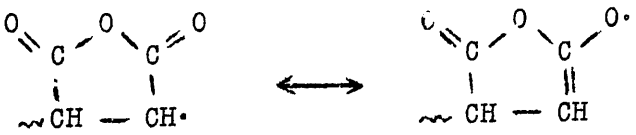
A study of Stuart models shows that the above transition state should be sterically strain-free. In view of the strong polarizing influence of the adjacent carboxylic acid proton on the ester carbonyl oxygen, the energy of activation for formation of this transition state may well be lower than that for the corresponding Hurd and Blunck 6-membered ring. This could explain the experimental observation (Experimental

Section, p.127) that the onset temperature for A' scission of (V) was 50° lower than that for the simple diester, diethyl succinate.

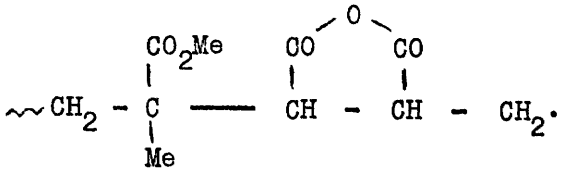
An alternative anhydride-forming route to the above, whereby ethanol is eliminated from a monoethyl maleate unit in the copolymer, must also be considered a formal possibility, although no ethanol could be detected in the volatile pyrolysate from (V). Nagel and Abelsdorff[108] have shown that diethyl phthalate decomposes thermally by the following major route:



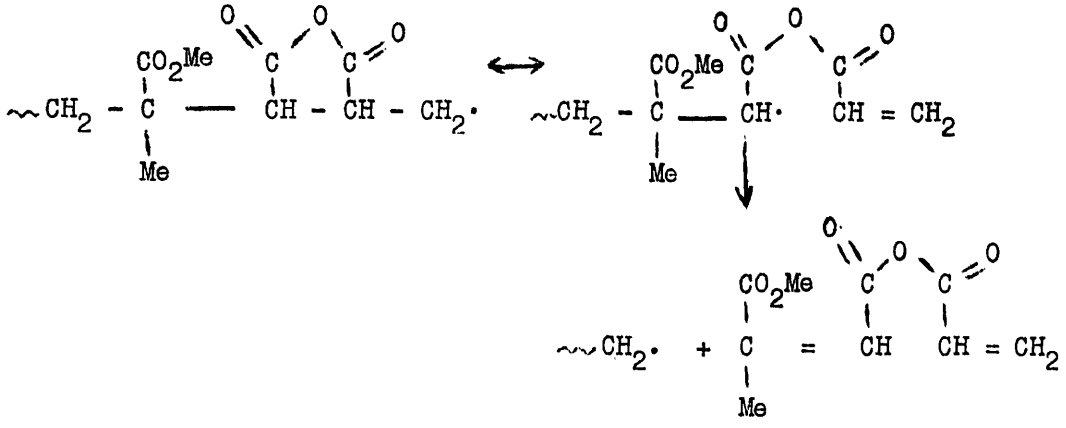
and <u>not</u> by successive A' scissions of the diester to phthalic acid which might then conceivably eliminate water to give the anhydride. Although no anhydride could be detected in the degraded copolymer, nor water in the volatile pyrolysate (infrared spectroscopy and anhydrous copper sulphate test respectively) it is possible that even minute amounts of anhydride formed in the copolymer chain may have a profound stabilizing influence[99] on the depolymerisation of (V). A possible mechanism of stabilization may be resonance between the radical structures shown: if the second structure contributes markedly, further depolymerisation of the macroradical should be disfavoured:



Alternatively, depolymerisation may yield at some stage the macroradical shown:



This macroradical should exhibit great reluctance to undergo possible further depolymerisation as follows:



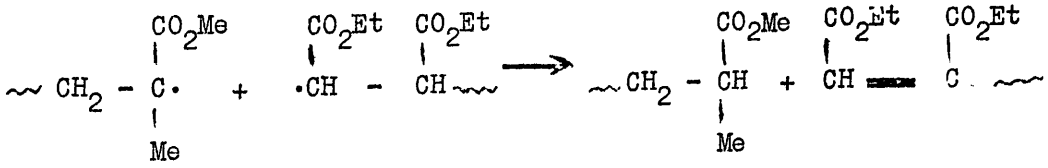
Polymerisation and depolymerisation are essentially reactions which normally exist in equilibrium. Since the intermediate radical shown is always associated with an unsaturated structure, and may be compared to an ordinary polymer radical, surrounded by a high monomer concentration, the equilibrium of the first reaction should be well over to the left. Depolymerisation would thus be inhibited, the radicals being destroyed ultimately in some other process.

The low extent of volatilization reached in the somewhat random degradation of (V) can thus be explained.

2.6 Termination of Degradation of (V)

In addition to the inhibitory termination process discussed in the preceding section, another kind of depolymerisation termination may occur for (V). For the thermal degradation at 220° of poly(methyl α-methylacrylate) of relatively high molecular weight (M_n greater than ca. 500,000), Grassie and Melville[86] attributed the experimentally observed gradual decrease in molecular weight to termination by disproportionation of pairs of degrading macroradicals before whole polymer molecules could be eliminated. The smaller polymeric residues thus left had a lowering effect on the molecular weight of the polymer. Every act of termination by disproportionation results in formation of a saturated and an unsaturated chain-end, the latter being capable of subsequent activation to initiate a degrading macroradical. Thus one 'active' chain end results from two that were originally present, and the number of degradable chain-ends in the system rapidly decreases to zero at the end of pyrolysis.

An analogous disproportionation termination mechanism may be proposed for the pyrolysis of (V) at 220-260°:



Although a considerable degree of combination appears to occur in the termination step of copolymerisation of diethyl maleate with methyl α-methylacrylate at 60°, disproportionation, which is essentially

a transfer process, is strongly favoured at the elevated temperatures of pyrolysis. The disproportionation termination mechanism as written above governs the interaction of pairs of dissimilar radicals: it could also formally occur between pairs of like radicals. It is practically impossible, however, to determine whether exclusive cross-termination occurs during pyrolysis (as for copolymerisation), or whether termination occurs partly between pairs of like radicals.

2.7 Conclusions

Several salient points emerging from the results of pyrolysis of (V) at 220 - 260° are presented below:

(i) Depolymerisation of (V) at 220° (and presumably also at 260°) is initiated at the chain-ends, probably by chain scission in the region of each terminal double bond to an allyl-type radical and a macroradical which then immediately undergoes depolymerisation.

(ii) The shape of the molecular weight versus percentage volatilization curves for (V) at 220 - 260° would indicate the presence of a large random factor, although the extent of volatilization ultimately reached (ca. 45 - 55%) is lower than that observed by other workers (ca.100%) for the random thermal degradation of poly(methyl ∝-methylacrylate) at 300° and higher temperatures. The randomness observed for (V) at 220 - 260° is attributed to intermolecular chain transfer followed by chain scission of the copolymer molecule at the point attacked. A stabilizing influence, possibly intramolecular formation of occasional

anhydride units, develops in the degrading system, inhibiting complete depolymerisation of the copolymer from the chain-ends formed after scission. This would account for the unexpectedly low extent of volatilization reached in the somewhat random process.

(iii) Although branching of (V) could theoretically introduce a considerable random factor to the degradation process, physical measurements made on the copolymer before pyrolysis detected no marked degree of branching.

(iv) It is apparent from the experimental results that chain scission of (V) does not occur at every diethyl maleate unit in the copolymer [c.f. the degradation of poly (acrylonitrile-methyl α-methylacrylate)], and hence it is unlikely that studies of the molecular weight changes that take place during the pyrolysis of copolymers could be used as the basis of a general method of checking monomer reactivity ratios.

Applying these results to the pyrolysis of the cross-linked resin (IV), it may be deduced that, in the resin, depolymerisation starts at the terminal double bonds of the loose polyaddition chains, but is not normally terminated at the first attachment to a fumarate unit in the polyester chain. More likely, the unzippering process proceeds right through the fumarate units of several successive polyester chains. If the 'anhydride theory' proposed above for the pyrolysis of (V) is correct, there is the formal possibility that at those polycondensation chain-ends in (IV) which are terminated by a cross-linked fumaric acid unit, pyrolytic anhydride formation may eventually occur and thus inhibit

further depolymerisation beyond this point. This process is probably unimportant in the pyrolysis of (IV), however, for two reasons:

(i) Formation of the 10-membered cyclic transition state may well be sterically hindered by the rigidity of the macromolecule,

and (ii) The relatively small number of points of cross-linking which have the necessary structure for eventual low-temperature anhydride formation reduces the importance of inhibition in the resin on purely statistical grounds.

The chain transfer process observed in the pyrolysis of (V) at 220 - 260° may be somewhat suppressed in the resin (IV). Each act of transfer almost certainly requires close approach of a degrading macro-radical to a labile tertiary hydrogen atom attached to the polyaddition chain backbone. In (IV), every tertiary hydrogen atom is located at a point of cross-linking between a polyester chain and a polyaddition chain. A considerable 'shielding' effect around each tertiary hydrogen atom might thus arise, preventing approach of an attacking free-radical and thus decreasing the efficiency of chain transfer.

Another predictable effect, peculiar to the pyrolysis of (IV), might arise from the lower mobility of degrading polyaddition chain-ends within the tightly-bound macromolecular network. This would be expected to lead to a lower rate of chain termination and hence a higher rate and mean kinetic chain-length of depolymerisation than would exist for (V) pyrolysed under the same conditions - i.e. a kind of

'Trommsdorf effect' applied to depolymerisation. Although necessarily hypothetical, the above considerations make it clear that direct depolymerisation of the polyaddition chains in (IV) should be by far the most important process in the degradation of the resin at temperatures below 300°, this being the onset temperature for random scission of the internal C-C bonds of the poly(methyl ∝ methylacrylate) chains.

To prevent depolymerisation of the polyaddition chains in (IV), three modifications of the resin can be suggested:

(i) An inhibitor, such as 1:4-diaminoanthraquinone, might somehow be incorporated in the resin, thus stabilizing it to temperatures up to 220°. The dispersion of the inhibitor throughout the resin is, however, problematic. Inhibitor cannot be added to the resin before curing since it would, of course, inhibit the cross-linking process. The fully cured resin is, moreover, highly insoluble in organic solvents.

(ii) Saturation of the terminal double bonds of (IV), e.g. by hydrogenation, might somehow be achieved, although this is of course subject to the same solubility difficulties as would be encountered in (i).

(iii) Cross-linking in the presence of a chain transfer solvent might have the effect of reducing the ratio of unsaturated to saturated chain-ends in the resin. This technique, devised by Grassie, was successfully employed by the latter to vary the proportion of terminal double bonds in poly(methyl ∝-methylacrylate).[109]

3. EXPERIMENTAL

3.1 Preparation of Polymeric Pyrolysands

The polymeric pyrolysands were prepared from carefully purified monomers, polymerisation at 60° being initiated by the thermal decomposition of benzoyl peroxide (0.1 mole %).

3.1.1 Purification of Benzoyl Peroxide

'Analar' benzoyl peroxide was purified by recrystallisation from chloroform-methanol in the cold. The white crystals were filtered off, washed with a little methanol, and dried by suction at the filter pump. The purified benzoyl peroxide was stored in a desiccator over calcium chloride before use.

3.1.2 Purification of Methyl α-Methylacrylate

To remove inhibitor, commercial methyl α-methylacrylate (ex I.C.I. Ltd.) was shaken with successive portions of 10% aqueous sodium hydroxide solution until the sodium hydroxide layer was colourless. The monomer was then shaken thoroughly two or three times with distilled water to remove any residual sodium hydroxide, dried over calcium chloride, and further purified by distillation under reduced pressure, the clear fraction b.25°/14 mm. being collected for use. The purified methyl α-methylacrylate was stored in a refrigerator until required.

3.1.3 Preparation and Purification of Diethyl Maleate

Diethyl maleate was prepared by esterification of maleic acid, following the phase separation method of Klostergaard[110]. Maleic acid (232 g. and ethanol 230 g.) were refluxed for 15 min. with a catalytic amount of

conc. hydrochloric acid, followed by the addition of the ester solvent toluene (244 ml.) under continued reflux. Additional conc. hydrochloric acid (25 ml.) was added, followed by anhydrous calcium chloride (50 g.). The whole mixture was refluxed overnight. The toluene layer was separated, washed with a little water, dried over anhydrous sodium sulphate, and then fractionated. Diethyl maleate (301 g., b.105-6/14 mm.) was obtained in 87% yield on re-fractionation of the product.

3.1.4 Preparation of Poly(diethyl maleate-methyl α-methylacrylate) (Mn = 471,000)

Copolymerisation of diethyl maleate and methyl α-methylacrylate was effected in a cylindrical Pyrex glass vessel of ca. 300 ml. capacity, containing an expansion bulb just below the sealing constriction. The initiator was introduced into the vessel as a standard solution in chloroform, the solvent being completely evaporated off under vacuum before adding the comonomers. The ratio of the comonomers was chosen so as to yield an initial copolymer of methyl α-methylacrylate : diethyl maleate ratio of 18:1, the reactivity ratios being 20 and 0 respectively[97].

A charge of diethyl maleate (201 g.) and methyl α-methylacrylate (99.3 g.) was added to the reaction vessel containing 0.522 g. benzoyl peroxide. The contents were thoroughly degassed, sealed off under high vacuum, and the vessel allowed to stand for 1 hr. in a thermostatic tank at 60°, during which time a low degree of copolymerisation occurred, as indicated by a slight increase in the viscosity of the system.

The reaction vessel was broken open, and its contents slowly poured

into an excess of methanol with vigorous stirring to precipitate the copolymer. After decanting the supernatant liquid, the gelatinous white precipitate was rendered amorphous by washing with fresh methanol. The crude copolymer was roughly dried, redissolved in acetone, and re-precipitated by pouring into an excess of methanol, with brisk stirring. After decanting and discarding the supernatant liquid, precipitation was completed by the successive addition and decantation of two or three batches of fresh methanol, with continued vigorous stirring.

The amorphous copolymer was allowed to dry in air for 4 hrs., before being ground to a particle size of less than 80 mesh. The powdered copolymer was finally dried in a steam oven for 24 hrs: yield 10.5 g., or ca. 10% (based on methyl α-methylacrylate).

3.1.5 Preparation of Poly(methyl α-methylacrylate) ($\bar{M}_n$ ≈ 717,000).

Methyl α-methylacrylate was polymerised at 60° in bulk (0.1 mole % benzoyl peroxide as initiator) under essentially the same experimental conditions as described above for poly (diethyl maleate-methyl α-methyl acrylate). Purification of the resultant polymer was similarly achieved. A 100 g. batch of monomer yielded ca.4.5 g. of the polymer in powder form.

3.1.6 Preparation of Poly(diethyl fumarate-methyl α-methylacrylate).

Poly (diethyl fumarate-methyl α-methylacrylate) was prepared under the same experimental conditions as for poly(diethyl maleate-methyl α-methylacrylate) (see above). The reactivity ratios for the monomer

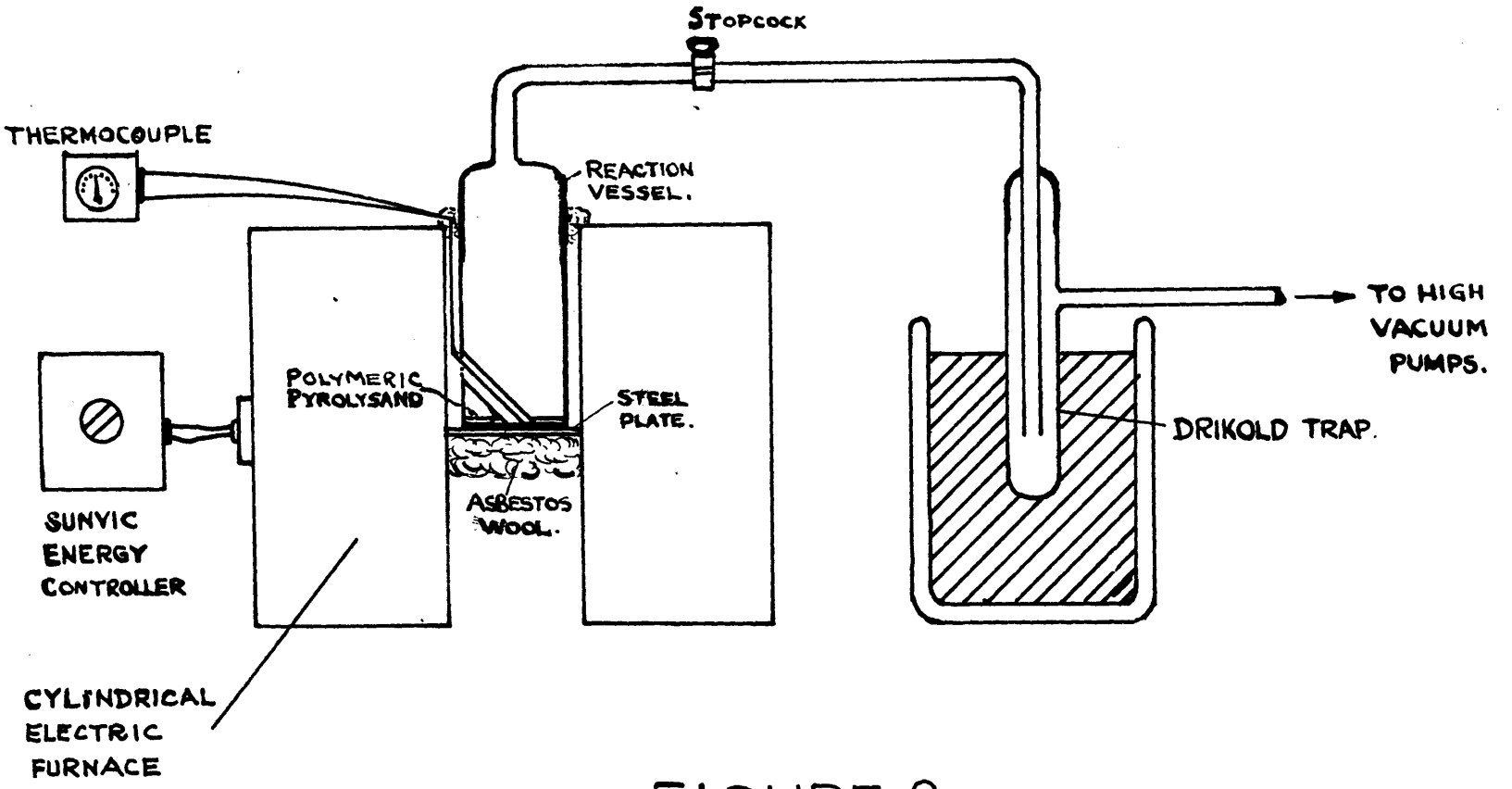


FIGURE 8.

APPARATUS FOR STATIC PYROLYSIS OF HIGH POLYMERS (NOT TO SCALE).

pair diethyl fumarate and methyl α-methylacrylate do not appear to have been reported in the literature, but, since pyrolysis of this copolymer was only of qualitative interest, its exact composition did not have to be found.

3.2 Apparatus and Procedure for Pyrolysis of Polymeric Substances

The apparatus used for the pyrolysis of polymeric materials is illustrated in Fig. 8. The cylindrical reaction vessel (height 5 in., I.D. $1\frac{3}{4}$ in.) was constructed of Pyrex glass, and contained a thermocouple pocket located so that the hot junction of the chromel-alumel thermocouple just came into contact with the flat base of the vessel. During a run, the reaction vessel was heated to within $\pm 2^{\circ}$ of the required temperature in a cylindrical external heater regulated by a Sunvic energy controller. The base of the vessel rested on a steel disc, the whole being kept in position (and thermally insulated) by asbestos packing. The vessel was evacuated by means of a high vacuum oil pump, used in conjunction with a mercury diffusion pump.

Before pyrolysis, the specimen of powdered polymer (ca. 0.5 g.) was spread as evenly as possible over the bottom of the reaction vessel. The degree of volatilization was determined by weighing the vessel and its contents on a semimicro balance before and after each run. Volatile products of pyrolysis were condensed in a cold trap, cooled in Drikold-acetone, situated between the reaction vessel and the pumps.

To prevent oxidation, the pyrolysis vessel containing the polymer specimen was slowly and carefully evacuated and sealed off at the stopcock

before being placed in the heater, which had previously been maintained at the required temperature for ca.2 hr. With the vessel in position, the electrical input to the heater was increased by a predetermined amount until the specimen reached the desired temperature, which took ca.5 min. At this point, the stopcock was opened to high vacuum and pyrolysis allowed to commence. At the end of the run, the stopcock was closed and the evacuated reaction vessel immediately removed from the heater and quickly cooled down to room temperature by standing in a current of cold air. The vessel was then opened to atmosphere and finally weighed. The results of pyrolysis of polymeric substances are summarized in Table 3.

3.3 Preparation of Polymer Samples for Physical Measurements

After each run, the polymeric residue was completely dissolved from the reaction vessel in a little acetone, and the solution passed through a fine sintered-glass filter. The polymer was then re-precipitated in amorphous form by pouring into an excess of methanol with vigorous stirring, followed by washing with successive batches of fresh methanol. The amorphous polymer was dried for 24 hr. at 80° before being re-dissolved in pure benzene and 'freeze-dried' for 12 hrs. on the vacuum line. The polymer was thus obtained as a porous white solid, readily soluble in benzene and chloroform.

3.4 Molecular Weight Measurements

(a) Osmotic Method

Number-average molecular weight measurements were made using the

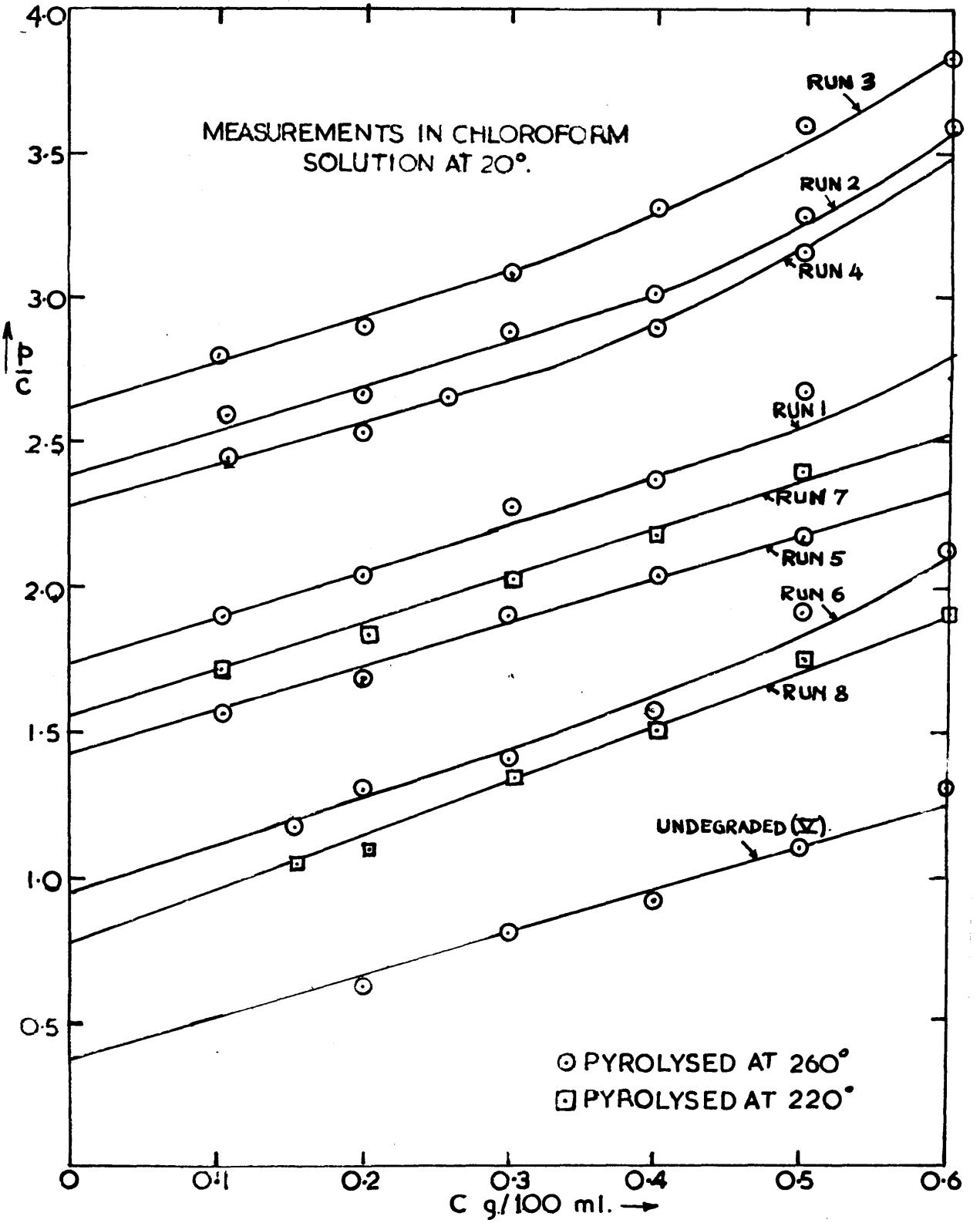


FIGURE 9.

OSMOTIC MOLECULAR WEIGHT DETERMINATIONS FOR COPOLYMER (V) AT VARIOUS STAGES OF THERMAL DEGRADATION.

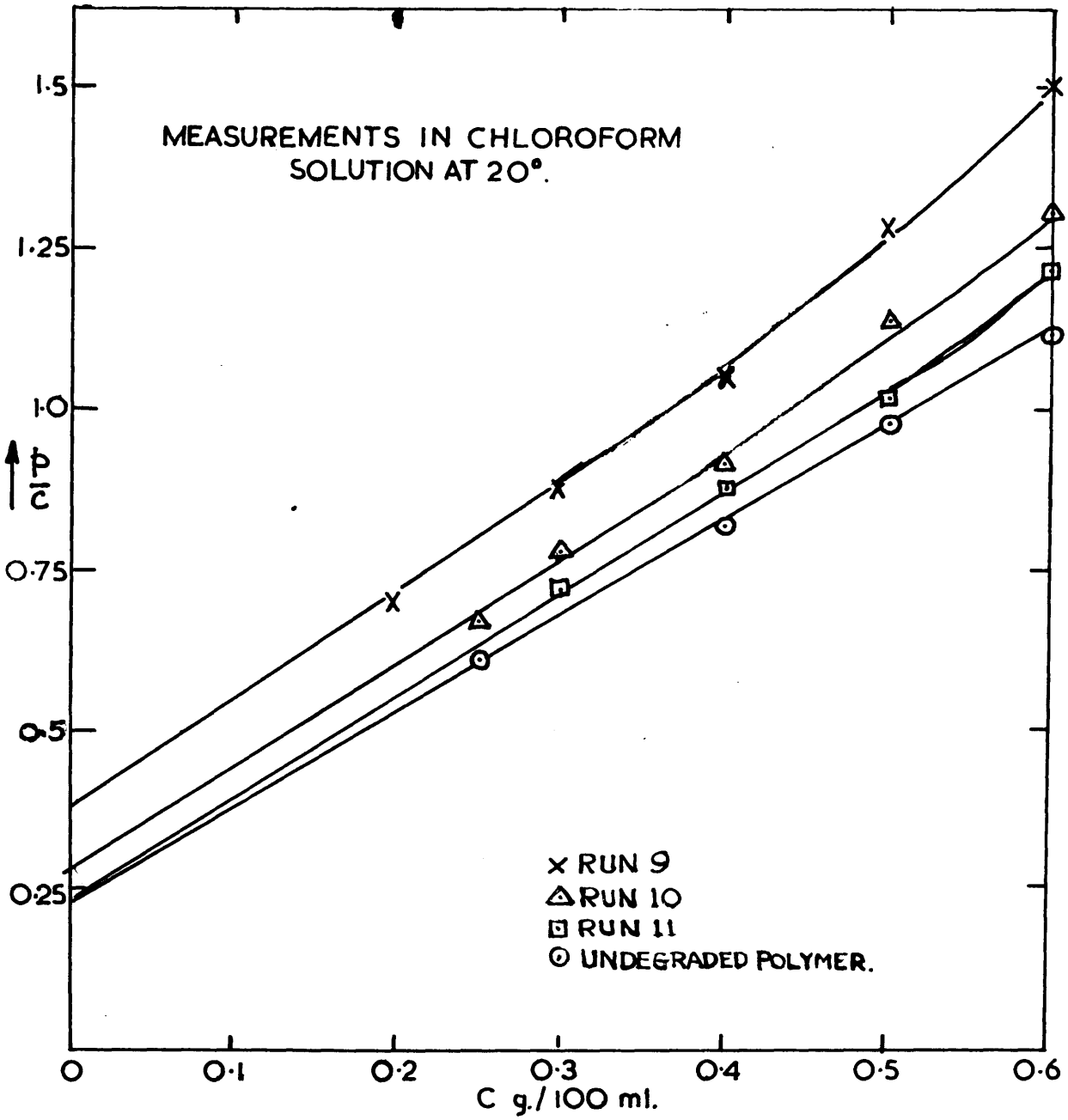


FIGURE 10.

OSMOTIC MOLECULAR WEIGHT DETERMINATIONS FOR POLY-(METHYL α-METHYLACRYLATE) AT VARIOUS STAGES OF THERMAL DEGRADATION AT 260°.

Pinner-Stabin-type osmometer[110] (Polymer Consultants Ltd.) with membranes prepared from undried cellulose. Measurements were made in chloroform (Analar) solution at 20 $\pm$ 0.005° for a series of concentrations obtained by successive dilutions of the original polymer solution. The osmotic pressure in the system attained its equilibrium value in ca. 12 hrs. The osmotic data for poly (diethyl maleate-methyl α-methylacrylate) and poly (methyl α-methylacrylate) at various stages of thermal degradation at 220-260° are given in Table 4. For each sample, the ratio of $\frac{p}{c}$ was plotted against c (where p is the osmotic height in cm. of solution, and c is the concentration in g./100 ml. of solution), and the limiting value at zero concentration determined by graphical extrapolation (Figs. 9 and 10).

Hence the number-average molecular weight, Mn, for each polymer sample was calculated from the equation

$$\left(\frac{\pi}{C}\right)_{c=o} = \frac{RT}{Mn}$$

where π is the osmotic pressure in atm.

C is the polymer concentration in g./litre.

R is the gas constant

= 0.082 litre atm./°C x mole

and T is the absolute temperature.

The following example serves to illustrate the calculation of M_n.

For the undegraded copolymer (V),

$$\left(\frac{p}{c}\right)_{c=0} = 0.35$$

$$\therefore \quad \left(\frac{\pi}{c}\right)_{c=0} = \frac{0.35 \times 1.502}{76.0 \times 13.59 \times 10}$$

$$\text{Hence } M_n = \frac{0.082 \times 293 \times 76.0 \times 13.59 \times 10}{0.35 \times 1.502}$$

$$= 471{,}000$$

(b) Intrinsic Viscosity Method

All measurements of intrinsic viscosity were made at 20 ± 0.005° in benzene solution, in a viscometer of the Ubbelohde type. This has the advantage that measurements are independent of the amount of solution in the viscometer, successive dilutions being made simply by measuring a known volume of solvent into the viscometer. Before use, the viscometer was steeped overnight in chromic acid mixture, washed with distilled water, rinsed with acetone, and dried in a warm oven.

The viscosimetric data are given in Table 5. For each specimen, $\frac{\eta_{sp}}{c}$ was plotted against c (where η_{sp} is the specific viscosity of a solution of concentration c g./100 ml.), and the limiting value at zero concentration (the intrinsic viscosity, $[\eta]$) determined by graphical extrapolation (Fig. 7).

(c) Light-scattering Method

The weight-average molecular weight (Mw) of the 18:1 copolymer (V) was determined by light-scattering measurements, made using the S.O.F.I.C.A machine, whereby the relative intensity of the scattered light from

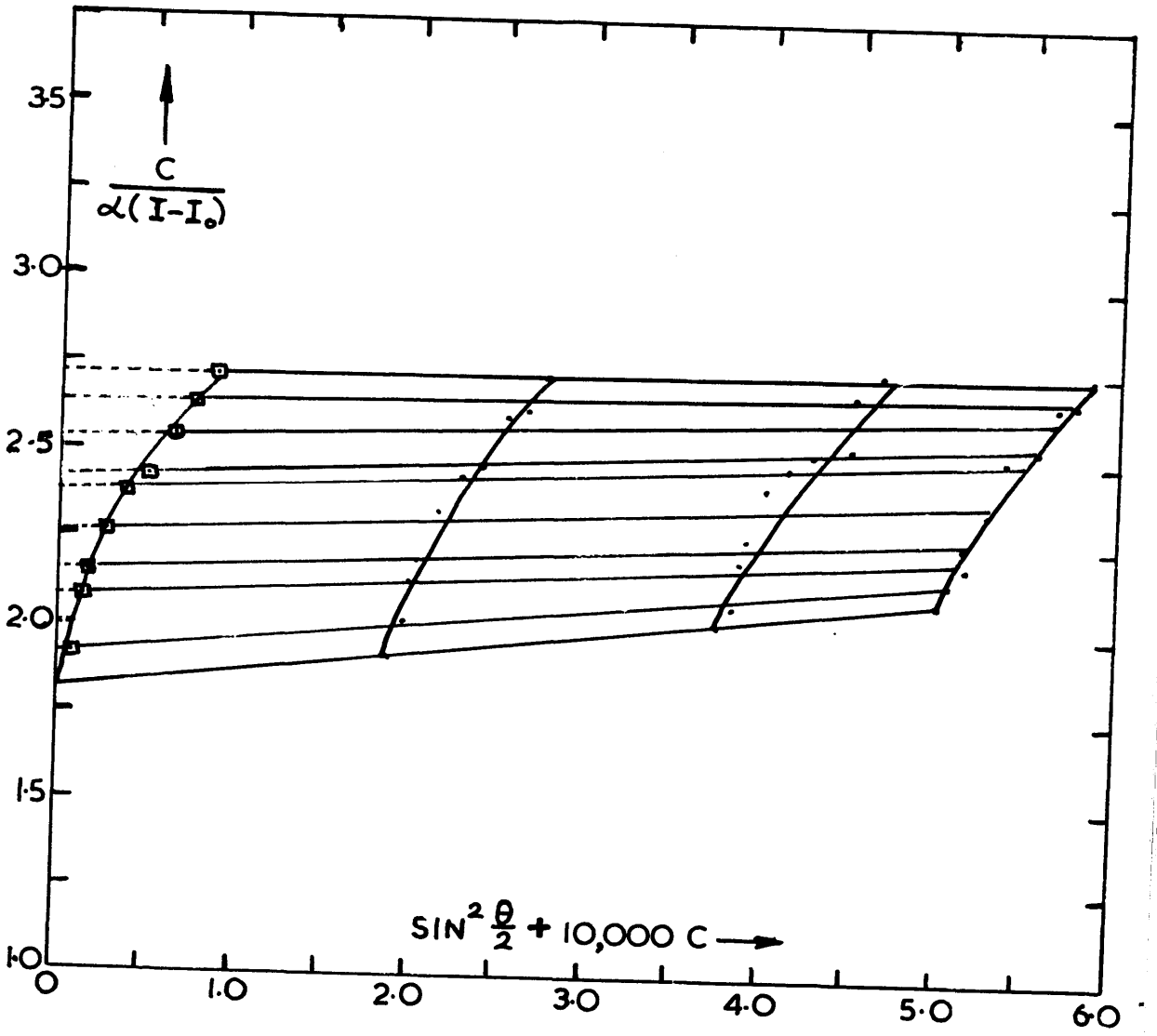


FIGURE 11.

ZIMM PLOT FOR UNDEGRADED COPOLYMER (V)

solutions of the copolymer was measured as a function of angle and concentration. Monochromatic light of wavelength 5,460°A (mercury green line) was used. Acetone solutions of the copolymer were rendered as dust-free as possible by passage through a No. 5 sintered glass filter.

For each of a series of solutions of concentration c g./ml., the relative intensity of light, $\alpha (I-I_o)$, was measured as a function of the angle of measurement θ, where I is the intensity of light transmitted by the solution at any given angle, I_o is the intensity of light transmitted by the pure solvent at the same angle, and α is a factor, depending on the angle of measurement, which reduces the scatter to that from the minimum volume. The data thus obtained (Table 6) were treated in the form of a Zimm plot (Fig. 11). For each concentration, $\frac{c}{\alpha(I-I_o)}$, henceforth abbreviated to $\left(\frac{c}{I}\right)$, was plotted against $(\sin^2 \frac{\theta}{2} + Kc)$ where K is an arbitrary constant, (here 10,000), chosen for convenience in plotting. The intercept on the abscissa, obtained by extrapolation to zero angle and zero concentration, $\left(\frac{c}{I}\right)_{\theta, c=o}$, was measured, and the weight-average molecular weight, M_w, calculated by substitution of this value in the characteristic equation for the instrument:

$$\frac{1}{M_w} = 0.506 \; I_B \left(\frac{dn}{dc}\right)^2 \left(\frac{c}{I}\right)_{\theta,\, c=o}$$

where I_B (= 100) is the value of $\left(\frac{c}{I}\right)$ for pure benzene, by means of which the instrument was calibrated, and $\left(\frac{dn}{dc}\right)$ is the rate of change of

refractive index with concentration of (V) in acetone solution (measured by the Pulfrich refractometer).

Thus, for the sample of (V) studied,

$$\frac{1}{M_w} = 0.506 \times 100 \times (0.11)^2 \times 1.81 \times 10^{-6}$$

whence $M_w = 828,000$.

3.5 Measurement of Onset Temperature

The onset (or threshold) temperatures at which competing depolymerisation and A' scission of the 18:1 copolymer (V) make their first appearance, under arbitrary standard conditions, have been determined by a simple technique devised by Mackinnon[55]. A small amount (ca.0.5 g.) of the copolymer was placed in a Pyrex glass reactor, whose temperature was slowly raised at a controlled rate (ca. 1°/min.). Volatile products were carried by a slow stream of nitrogen into an optical cell, traversed by a beam of light and containing a very dilute solution of bromine in carbon tetrachloride. The change in colour intensity produced by the onset of breakdown was detected by a photo-cell. To distinguish between the onset of depolymerisation of (V) and its A' scission reaction, the lowest temperature (170°) at which a detectable amount of unsaturated product was evolved from (V) was taken as the onset temperature of depolymerisation, presuming the product being evolved to be methyl α-methylacrylate. To remove methyl α-methylacrylate from the nitrogen gas stream during determination of the onset temperature of A' scission, a cold trap, cooled in Drikold-acetone, was placed between the reactor and the optical detection system, thus permitting specific detection of

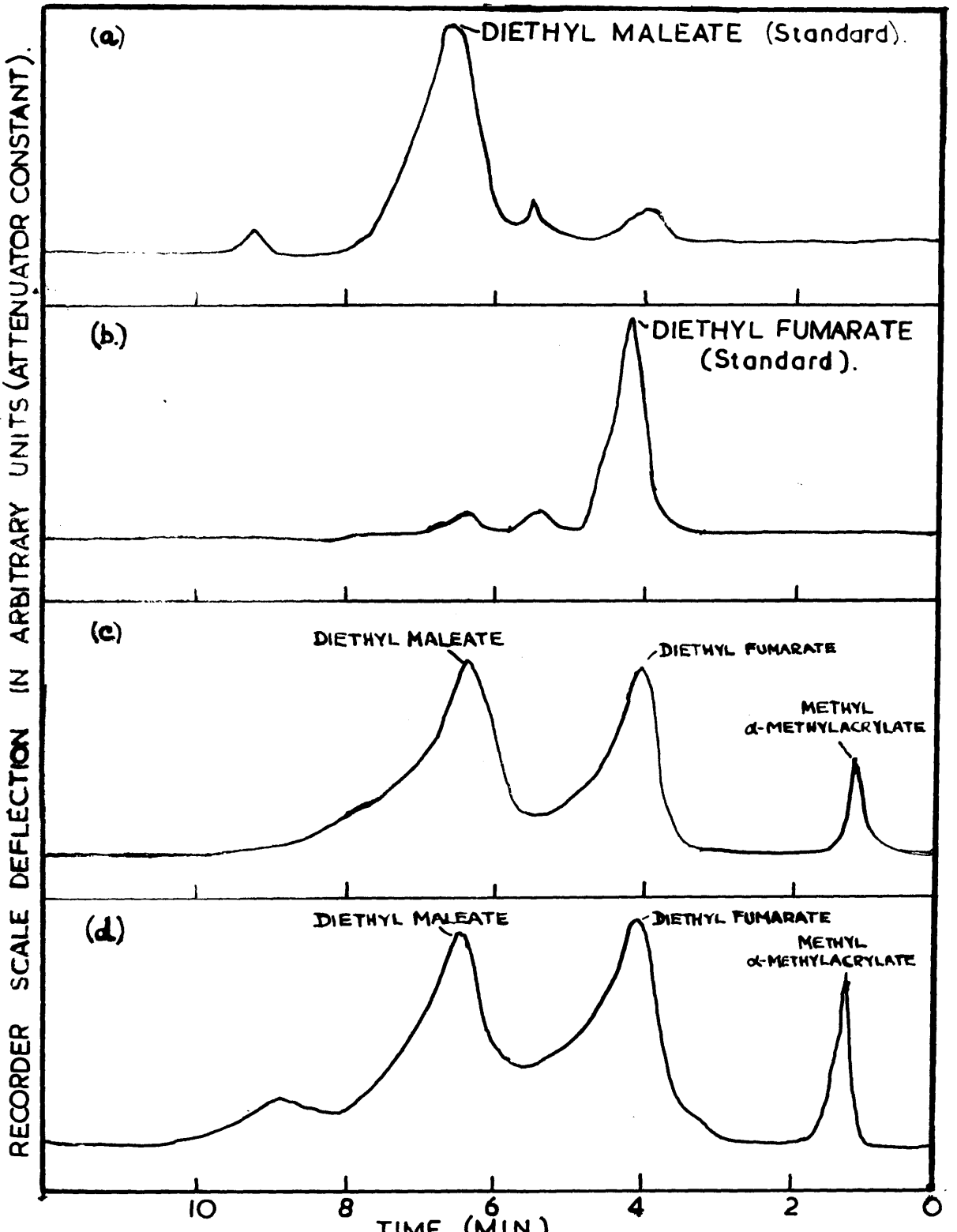


FIGURE 12.

VAPOUR PHASE CHROMATOGRAMS OF HIGH-BOILING PYROLYSATE FRACTIONS FROM (c) Poly(diethyl fumarate-methyl-α-methylacrylate). and (d) Poly(diethyl maleate-methyl-α-methylacrylate), with standards (a) & (b).

the A' scission product ethylene to be achieved. The onset temperature of A' scission of (V) was thus found to be 280°.

3.6 Vapour-phase Chromatography

The volatile products of pyrolysis of the polymeric substances described in Part II of this thesis were examined by means of the Pye Argon Chromatograph, Cat. No. 12001, which is equipped with a highly sensitive ionization detection device. The column used, of length 4 ft. and bore 4 mm., was packed with 10% w/w Apiezon L stopcock grease on celite (100 mesh). A column temperature of 150° was used, with an argon flow rate of ca. 1.95 l./hour. The detector voltage was 1,000 volts throughout. The sample (0.1 µl.) was introduced into the column by means of a micropipette.

Satisfactory quantitative analysis of the various volatile pyrolysates could not be achieved, since, although all of the methyl α-methylacrylate condensed in the Drikold trap, the relatively involatile maleic and fumaric components were found to condense out partly in the Drikold trap, partly in the glass inlet tube of the latter, and even inside the stopcock of the reaction vessel. Accurate sampling of the total volatile pyrolysates was thus prevented.

Qualitative vapour-phase chromatograms of the pyrolysates from poly(diethyl maleate-methyl α-methylacrylate) and poly(diethyl fumarate-methyl α-methylacrylate) are represented in Fig. 12, together with reference standards for comparison.

TABLE 3

PERCENTAGE DEGRADATION FOR EACH RUN

Run No.	Pyrolysand	T°C	Duration	Initial Wt.	Final Wt.	Loss in Wt.	Percentage Volatilization
1	(V)	260°	10.0 hr.	0.521 g.	0.291 g.	0.230 g.	44.2%
2	(V)	260°	4.0 hr.	0.519 g.	0.277 g.	0.242 g.	46.6%
3	(V)	260°	1.5 hr.	0.509 g.	0.318 g.	0.191 g.	37.6%
4	(V)	260°	6.0 hr.	0.505 g.	0.294 g.	0.211 g.	41.8%
5	(V)	260°	0.5 hr.	0.501 g.	0.428 g.	0.073 g.	14.5%
6	(V)	260°	0.5 hr.	0.500 g.	0.448 g.	0.052 g.	10.4%
7	(V)	220°	20.0 hr.	0.497 g.	0.231 g.	0.266 g.	53.5%
8	(V)	220°	9.0 hr.	0.513 g.	0.372 g.	0.141 g.	27.5%
9	poly MMA	260°	3.5 hr.	0.503 g.	0.256 g.	0.247 g.	48.0%
10	poly MMA	260°	1.25 hr.	0.494 g.	0.375 g.	0.119 g.	24.1%
11	poly MMA	260°	0.75 hr.	0.502 g.	0.458 g.	0.044 g.	8.8%
12	(V) + Cu (25% w/w)	260°	4.0 hr.	0.687 g.	0.468 g.	0.219 g.	42.5%
13	(V) + Caledon Gold Orange 3G (2% w/w)	260°	1.5 hr.	0.495 g.	0.443 g.	0.052 g.	10.5%
14	(V) + 1:4-dibenzamido-anthraquinone (2% w/w)	260°	1.5 hr.	0.488 g.	0.301 g.	0.187 g.	38.4%
15	(V) + 1:4-diaminoanthraquinone (equimolar)	220°	17.0 hr.	0.492 g.	0.333 g.	0.159 g.	32.3%
16	(V) + 1:4-diaminoanthraquinone (2% w/w)	220°	9.0 hr.	0.523 g.	0.520 g.	0.003 g.	0.6%
17	poly(diethyl fumarate-methyl α-methylacrylate)	260°	1.5 hr.	0.488 g.	0.301 g.	0.187 g.	38.4%

TABLE 4

OSMOTIC DATA: CHLOROFORM SOLUTION AT 20°

Conc. c (g/100 ml.)		Height p (cm.)	$\frac{p}{c}$; Intercept, I		Mn
(V)	0.60	0.802	1.33		
	0.50	0.551	1.10		
	0.40	0.365	0.91		
	0.30	0.243	0.81	0.35	471,000 = 100% original
	0.20	0.123	0.62		
Run 1					
	0.50	1.321	2.64		
	0.40	0.948	2.37		
	0.30	0.681	2.27	1.75	93,700 = 19.9% original
	0.20	0.410	2.05		
	0.10	0.190	1.90		
Run 2					
	0.60	2.153	3.59		
	0.50	1.637	3.27		
	0.40	1.199	3.00	2.41	68,300 = 14.5% original
	0.30	0.867	2.89		
	0.20	0.534	2.67		
	0.10	0.258	2.58		
Run 3					
	0.68	2.339	3.90		
	0.50	1.801	3.60		
	0.40	1.324	3.31	2.62	63,100 = 13.4% original
	0.30	0.927	3.09		
	0.20	0.582	2.91		
	0.10	0.284	2.84		
Run 4					
	0.50	1.581	3.16		
	0.40	1.158	2.90		
	0.25	0.667	2.67	2.35	70,200 = 14.9% original
	0.20	0.509	2.55		
	0.10	0.245	2.45		

TABLE 4 (continued)

Conc. c (g/100 ml.)	Height p (cm.)	$\frac{p}{c}$; Intercept, I	Mn
Run 5			
0.50	1.09	2.18	
0.40	0.819	2.05	
0.30	0.571	1.90 } 1.40	117,800
0.20	0.339	1.70	= 25.0% original
0.10	0.157	1.57	
Run 6			
0.60	1.267	2.11	
0.50	0.965	1.93	
0.40	0.637	1.59	
0.30	0.426	1.42 } 0.95	173,200
0.20	0.259	1.30	= 36.8% original
0.15	0.179	1.19	
Run 7			
0.50	1.219	2.42	
0.40	0.875	2.19	
0.30	0.612	2.04 } 1.58	104,600
0.20	0.368	1.84	= 22.2% original
0.10	0.173	1.73	
Run 8			
0.60	0.146	1.91	
0.50	0.881	1.76	
0.40	0.604	1.51	
0.30	0.405	1.35 } 0.79	208,500
0.20	0.224	1.12	= 44.3% original
0.15	0.157	1.05	
Run 9			
0.60	0.899	1.50	
0.50	0.640	1.28	
0.40	0.420	1.05 } 0.38	433,000
0.30	0.261	0.87	= 60.5% original
0.20	0.141	0.70	
Run 10			
0.60	0.793	1.32	
0.50	0.565	1.13	
0.40	0.368	0.92 } 0.28	591,000
0.30	0.234	0.78	= 82.5% original
0.25	0.168	0.67	

TABLE 4 (continued)

Conc. c. (g/100 ml.)	Height p (cm.)	$\frac{p}{c}$; Intercept, I	Mn .
Run 11			
0.60	0.738	1.23	
0.50	0.515	1.03	
0.40	0.353	0.88	0.23
0.30	0.219	0.73	717,000 = 100% original
Methyl α-methylacrylate starting material			
0.60	0.667	1.12	
0.50	0.489	0.98	
0.40	0.328	0.82	
0.30	0.209	0.72	0.23
0.25	0.152	0.61	717,000 = 100% original

TABLE 5

INTRINSIC VISCOSITY $[\eta]$ IN BENZENE SOLUTION AT 20°

Pure Solvent Flow Time = 72.4 secs.

Conc. c (g/100 ml.)	t (sec.)	η_r	η_{sp}	$\frac{\eta_{sp}}{c}$; $\left[\frac{\eta_{sp}}{c}\right]_{c \to 0}$
Copolymer (V)				
0.51	128.9	1.78	0.78	1.53
0.40	115.8	1.60	0.60	1.50
0.34	108.6	1.50	0.50	1.47
0.23	97.0	1.34	0.34	1.48
				1.45
Run 8				
0.46	109.2	1.51	0.51	1.11
0.40	102.8	1.42	0.42	1.05
0.27	92.7	1.28	0.28	1.04
0.23	89.8	1.24	0.24	1.04
				1.03
Run 13				
0.50	106.4	1.47	0.47	0.94
0.40	98.5	1.36	0.36	0.90
0.30	92.0	1.27	0.27	0.90
0.23	87.6	1.21	0.21	0.91
				0.87
Run 15				
0.50	100.7	1.39	0.39	0.78
0.40	94.8	1.31	0.31	0.78
0.34	92.0	1.27	0.27	0.79
0.23	85.4	1.18	0.18	0.78
				0.78
Run 16				
0.50	126.0	1.74	0.74	1.48
0.40	114.3	1.58	0.58	1.45
0.30	104.2	1.44	0.44	1.47
0.20	93.4	1.29	0.29	1.45
				1.43

TABLE 6

LIGHT-SCATTERING DATA : ACETONE SOLUTION AT 20°

α	0.286	0.370	0.471	0.693	0.905	1.00	0.905	0.693	0.471	0.370	0.286
θ	150	142.5	135	120	105	90	75	60	45	37.5	30
$\sin^2 \frac{\theta}{2}$	0.937	0.875	0.854	0.750	0.630	0.500	0.371	0.250	0.146	0.104	0.067
solvent I_o	116	83	64	45	37	35	38	49	73	101	150
				$c = 5.00 \times 10^{-4}$ g/ml.							
I	745	565	450	315	244	232	258	355	535	695	945
$(I-I_o)$	629	482	386	270	207	197	220	306	482	594	795
$(I-I_o)\alpha$	180	178.5	181.9	187	187.3	197	199	212	227	220	227.5
$10^6 \times C/(I-I_o)\alpha$	2.78	2.80	2.75	2.67	2.54	2.51	2.36	2.20	2.20	2.27	2.20
$\sin^2 \frac{\theta}{2} + 10{,}000\ C$	5.937	5.875	5.854	5.750	5.630	5.550	5.371	5.250	5.146	5.104	5.067
				$c = 3.75 \times 10^{-4}$ g/ml.							
I	590	450	355	246	194	184	205	276	425	560	780
$(I-I_o)$	474	367	291	201	157	149	167	227	352	459	630
$(I-I_o)\alpha$	135.7	135.8	137.0	139.3	142	149	151.2	155.2	165.7	170	180.2
$10^6 \times C/(I-I_o)\alpha$	2.76	2.76	2.74	2.69	2.54	2.52	2.48	2.42	2.26	2.20	2.08
$\sin^2 \frac{\theta}{2} + 10{,}000\ C$	4.787	4.625	4.604	4.500	4.480	4.250	4.121	4.000	3.896	3.854	3.817
				$c = 1.875 \times 10^{-4}$ g/ml.							
I	355	266	210	148	116	111	124	165	255	340	475
$(I-I_o)$	239	183	146	103	79	76	86	116	182	239	325
$(I-I_o)\alpha$	68.3	67.8	68.7	71.4	71.5	76	77.8	80.4	85.7	88.0	92.9
$10^6 \times C/(I-I_o)\alpha$	2.75	2.76	2.73	2.63	2.62	2.47	2.44	2.33	2.19	2.13	2.02
$\sin^2 \frac{\theta}{2} + 10{,}000\ C$	2.812	2.750	2.729	2.625	2.505	2.375	2.266	2.125	2.021	1.979	1.942

APPENDIX

Photopolymerisation of Methyl α-methylacrylate with Circularly Polarized Ultraviolet Light

1. Introduction

1.1 Asymmetric Influence of Circularly Polarized Light

In 1894, van't Hoff[112] suggested that optically active substances might be produced under the asymmetric influence of circularly polarized light, although he did not specifically mention ultraviolet light. Since then, several investigators have succeeded in realizing this idea experimentally; a few examples are given here:

Kuhn and Braun[113] irradiated alcoholic solutions of racemic ethyl α-bromopropionate in quartz vessels with right-and left-handed circularly polarized ultraviolet light. The solution acted on by the right-handed light developed a slight dextro-rotation and vice versa. Similar results were recorded by Mitchell[114], who was working with a solution of humulene nitrosite in ethyl n-butyrate.

Karagunis and Drikos[115] later showed that the addition of chlorine to certain triarylmethyl free radicals, in presence of circularly polarized light, produced optically active products. A total asymmetric synthesis was demonstrated by Davis and Heggie[116], who found that bromine combines with trinitrostilbene in a beam of circularly polarized light to form an optically active (dextrorotatory) product.

1.2 Isotactic Polymers

When a monomer of the type CH_2:CRR' ($R \neq R'$) is polymerised, a new asymmetric centre is created at every second carbon atom in the resulting polymer chain. Stereoisomerism is thus clearly possible, and is manifested in the three basic types of polymer designated by Natta *et al.*[117] as atactic, syndiotactic and isotactic polymer.

Atactic polymers are essentially amorphous. Each chain contains a random distribution of d- and l-configurations, which prevents regular, close packing of adjacent chains in a given specimen.

Syndiotactic polymers, on the other hand, exhibit a much higher degree of crystallinity, since each chain contains a regularly alternating sequence of d and l asymmetric carbon atoms.

Isotactic polymers, in which every asymmetric carbon atom in a given chain has the same configuration (d or l : there being equal numbers of each type of chain in a given sample) exhibit the commercially desirable properties associated with a high degree of crystallinity.

Certain catalysts, discovered by Natta[117] (e.g. titanium tetrachloride-trisobutylaluminium complex) are claimed to be highly stereoselective, producing syndiotactic and isotactic polymers. The mechanism of this type of heterogeneous catalysis has long been under discussion, but is not yet exactly known. It has been suggested[118] that the surface of the catalyst acts as a mould on which the growing polymer adopts a special configuration.

Under conditions of total solvation, anionic, low-temperature stereospecific polymerisation has been attributed[119] to small differences in the free-energies of the two possible transition states (each leading to formation of a unit of opposite optical rotation) resulting from interaction between the growing macroradical chain-end and the adding monomer molecule.

1.3 Objects of Research

The examples cited above show that circularly polarized light can exert a certain degree of influence over asymmetric synthesis. No consideration has hitherto been given to the possibility of stereospecific photopolymerisation of dissymmetrical olefins of the type $CH_2{:}CRR'$ ($R \neq R'$) by circularly polarized ultraviolet light, with production of crystalline polymers (perhaps isotactic). It was thought possible that during bulk polymerisation initiated by circularly polarized ultraviolet light, stereoselective formation of isotactic polymers might occur by an analogous mechanism to that proposed above for homogeneous stereospecific polymerisation; i.e. that the transition state of each successive monomer addition step might be influenced so as to result in stereospecific polymerisation.

The industrial advantages of such a process, if practicable, cannot be over-rated, since the costs of Natta catalysts are high. The present work was undertaken to investigate this possibility.

2. Discussion of Results

An optical system was constructed for the production of circularly polarized ultraviolet light (for details see Experimental Section) and a

high vacuum system set up for filling dilatometers with purified monomer.

Methyl α-methylacrylate was selected as being a suitable monomer for the present study, since polymerisation data was readily available. A trial experiment was run with methyl α-methylacrylate as monomer (no catalyst) contained in a cylindrical dilatometer made of Pyrex glass. During this run, lasting 13 days, polymerisation occurred to the extent of ca. 25%. No crystallinity could be detected by comparison of the X-ray diffraction pattern of a film made from the total resultant polymer (completely soluble in boiling heptan-4-one) with one of a film of the atactic polymer. It was therefore decided to attempt to reduce possible stray interference effects of the circularly polarized ultraviolet light caused by the curvature of the dilatometer walls. Dilatometers used in subsequent runs were constructed with built-in optically flat Pyrex glass discs.

Three runs, each lasting 13 days, were made in the thus modified dilatometers:

(i) using circularly polarized light (no catalyst);

(ii) using circularly polarized light (with azo-bis-isobutyronitrile as catalyst);

(iii) with plane polarized light.

In all of these runs, the resultant polymer was found to be completely soluble in boiling heptan-4-one, which suggests prima facie that no marked degree of crystallirity was produced. Distinction could not

readily be made between isotactic and atactic poly(methyl α-methyl-acrylate) by means of density measurements (isotactic d. = 1.19 g/ml.; atactic d. = 1.188 g./ml.) A film made from the total polymer from each run was subjected to X-ray diffraction. No difference in crystallinity could be detected by examination of the diffraction patterns. It is therefore concluded that circularly polarized ultraviolet light does not induce isotactic polymerisation of methyl α-methylacrylate.

3. Experimental

3.1 Polymerisation Apparatus

An optical system similar to that of Berson and Brown[120] was set up in a light-tight box, fitted with two light-baffled apertures through which adjustments could be made to the apparatus. All wall surfaces were painted matt black to minimise stray reflections. The only illumination was provided by a G.E.C. compact source mercury arc lamp, mounted in a black metal housing fitted with a Chance OX1 filter to isolate the 365 mμ line. Heat developed by the lamp was removed by means of an extractor fan mounted in a light-baffled funnel above the lamp housing.

A 6 in. collimating lens was placed in front of the source at its focal length. The collimated, monochromatic beam was polarized by reflection from a 6 x 9" plate of black glass. This plate was mounted in an adjustable clamp and rotated until the reflected beam was plane polarized. Plane polarization was tested by passing the beam through a Nicol prism on to a fluorescent screen, and was indicated by total extinction of the image on the screen when the Nicol prism was rotated

to the 'crossed' position. The plane-polarized beam was then passed through a specially constructed quarter-wave plate of thickness 0.0003 in. to achieve circular polarization. The emergent beam was tested for circular polarization with a similar quarter-wave plate, a Nicol prism and a fluorescent screen.

3.2 Purification of Monomer

Commercial methyl α-methylacrylate (ex I.C.I. Ltd.) was freed from inhibitor by shaking with aqueous sodium hydroxide solution, followed by washing with distilled water and drying over calcium chloride. The monomer was distilled under reduced pressure and the middle fraction collected for use. Final purification was achieved by distillation on the high vacuum line.

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